UNIVERSITY OF ALBERTA

THE EFFECT OF LIGHT ON SELECTED PROPERTIES OF PARYLENE C-COATED SILK FABRICS

BY

BONNIE G. HALVORSON

©

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE
DEPARTMENT OF CLOTHING AND TEXTILES

EDMONTON, ALBERTA
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Dear Bonnie,

Sorry to take so long getting back to you. You know how it goes!

In regard to the Windover Fabric, you may summarize as you wish from this paper. It has finally been published and I am enclosing the source information for you.

The source of the U.V. data is probably from a U.C.C. internal report or Spivak's paper which I also enclose for your reference.

You may use any of the diagrams and tables in your paper, that's what they are for.

If you would like to have a U.C.C. scientist proofread your draft and comment, I as well as Dr. Beach, would be willing to assist. Just let me know.

In any case, we would like to have copies of your work.

I hope all goes well with your work, and hope to see you at some future date.

Sincerely,

Bruce J Humphrey

Bruce J. Humphrey
Conservation Specialist

BJH:ras

Enclosures

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Yours sincerely,

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Editor

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Nancy Kerr
Dr. N. Kerr (supervisor)

Betty Crown
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Dr. M. Hollingsworth

Date: August 15, 1991

ABSTRACT

Consolidation of highly degraded silk artifacts is problematic for the textile conservator because there is no entirely satisfactory treatment method. One option recently introduced to the field of conservation is parylene C, a polymer whose unique gas-phase deposition method allows extremely thin (below 1 μm), highly conformal coatings to be applied.

For parylene C to be used successfully as a conservation treatment, the coating must not only have a positive initial effect, but must also resist degradation over time. In order to evaluate the long-term effect of light on parylene C-coated silk fabrics, the change in colour, flexural rigidity, tensile properties, and moisture regain after accelerated photochemical aging was measured, and the fabrics analyzed with SEM. The samples were aged by placing them in a xenon-arc Weather-Ometer: some samples were masked from the light, or protected by a UV filter (which excluded radiation with wave-lengths below 400 nm), while others were exposed to the full simulated daylight spectrum emitted by the xenon arc lamp.

The effect of the parylene C coating was found to depend on several factors including fabric construction, colour of dye, and the initial strength of the fabric. A thin coating (< 1 μm) on naturally aged silk fabric made highly deteriorated fabrics easier to handle, even though statistically significant differences in tensile properties could not be established in some cases. This thin coating also caused a noticeable stiffening of all fabrics tested, and a slight iridescent sheen was apparent on smooth-surfaced, dark-coloured samples.

The parylene coating retained its beneficial consolidating properties with exposure to visible light, but was not capable of slowing down the degradation of silk if wave-lengths below 400 nm were present. With exposure to UV

light, the thin coating yellowed noticeably, and became embrittled as revealed by SEM. It is therefore of paramount importance that artifacts consolidated with parylene C be protected from harmful ultraviolet radiation. Because parylene is an irreversible technique, the decision to coat a textile artifact with this polymer must be made carefully; however, for highly degraded silk artifacts for which there is no other viable option, this treatment may be appropriate.

ACKNOWLEDGEMENTS

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I wish to acknowledge the financial support of Union Carbide Corporation in providing funds for me to travel to the Nova Tran Laboratory in Clear Lake WI. Many thanks are due to Bruce Humphrey for his assistance in coating my samples, and for providing me with excellent resource material (and parylene-coated Big Bird feathers). Thanks also to Mr. Henry Yetter for taking the time to dig up answers to my questions.

The assistance provided by Elaine Bitner in operating the Weather-Ometer and countless other activities was greatly appreciated, as was the help of Linda Turner. I am also grateful for the assistance I received from the people in the statistical consulting office, especially Terry Taerum for his invaluable help in running the statistics on my data and thus making sense of all those numbers. Thanks also to George Braybrook for working his magic on the scanning electron microscope to produce such terrific photographs.

In addition, I need to extend heartfelt thanks to Joan, Nikki, Aileen, and the other CLTX grad students for always being there to 'talk textiles' or whatever else, and to the friendly folks in the geology department for their wonderful sense of fun. A very special thank-you goes to Stephen Prevec for his never-ending support and encouragement, and for always knowing the right thing to do or say. Finally, I wish to thank my parents for always encouraging me in whatever I decided to do.

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CHAPTER 1 INTRODUCTION

Justification and Statement of Purpose

Many museum collections contain artifacts made from silk. The conservation of highly degraded "shattered" silk is problematic and as yet there is no entirely satisfactory approach to treatment (Bogle, 1979). Often conventional stitching techniques cannot be utilized because the needle and sewing thread may break the fragile textile yarns. The use of adhesives for lamination, impregnation or application of a support backing increases the stiffness of the fabric, which may be unacceptable in some cases. The application of such a backing may also obscure important structural and historical information.

Recently, a vapour-polymerized coating called parylene C has shown promise in the field of artifact conservation. The coating is colourless, transparent, flexible, strong, highly conformal, and its method of application causes minimal stress to most substrates (Humphrey, 1984). The literature on its conservation applications reports sufficient success to warrant further research. "We are convinced that Parylene provides a means of dealing with the most fragile of materials so that they become effectively consolidated and strengthened" (Grattan, 1989, p. 16).

For parylene C to be used successfully as a conservation treatment, however, the coating must not only be beneficial initially, but must also be stable over long periods of time. The effects of photochemical aging on parylene-coated objects is especially important, as artifacts must be exposed to a certain amount of light for research or exhibit purposes. States Grattan, "The effect of light has not been studied so much and there is much we would like to know" (Grattan, 1989, p. 16). In the case of silk artifacts, the problem is compounded as the fibres themselves are highly sensitive to light, especially if weighting agents are present (Bogle, 1979).

In the area of textile conservation, parylene's effect on the flexibility, colour, tensile strength, and moisture absorbency of fabrics has only been partially analyzed. The work on parylene-coated silk done by Hansen and Ginell (1989) at the Getty Institute addresses some of these questions, but leaves room for expanded research. Their study tested parylene coated modern and naturally aged silk, as well as unsupported parylene films. Because Hansen and Ginell (1989) did extensive testing on modern silk, this fabric will not be included in the present study; artificially aged silk and naturally aged silk will be used.

The Getty research studied the effects of filtering out UV light on the colour of unsupported parylene films. The present study will determine the effect of these filters on change in colour and tensile properties of coated silk.

The historic silk used in the Getty study underwent accelerated aging before the coating was applied, but not after; change in properties were measured before and after coating only. Both the naturally and artificially aged coated samples in the present study will be exposed to simulated daylight, and the changes due to accelerated photochemical aging measured. In addition, this study will measure changes in moisture absorption and flexibility, properties not covered by the research at the Getty Institute.

The purpose of this research project is to determine the initial effects of the parylene-C coating on selected silk properties, and how these properties change after photochemical aging through exposure to simulated daylight of varying wave-lengths.

Objectives

The objectives of this study were:

1. to apply the parylene C coating to naturally and artificially-aged silk fabric;
2. to study the initial effects of the coating on selected silk properties: tensile strength, flexibility, colour, and moisture absorption;
3. to determine whether the selected properties change after exposure to simulated daylight, using a xenon-arc Weather-Ometer;
4. to determine whether the presence of a UV filter affects the change in properties of xenon-arc exposed coated silk; and
5. to observe the appearance of the parylene coating using scanning electron microscopy.

Definitions

For the purpose of this study:

Degradation: refers to gradual impairment with respect to some property, quality, or capability, or to the chemical breakdown of polymeric material into a less complex compound (Miller, 1986).

chemical degradation: refers to "processes which are induced under the influence of chemicals (eg. acids, bases, solvents, reactive gases etc.) brought into contact with polymers" (Schnabel, 1981, p. 14)

thermal degradation: occurs when "the polymer, at elevated temperatures, starts to undergo chemical changes without the simultaneous involvement of another compound" (Schnabel, 1981, p. 14)

photodegradation: "concerns the physical and chemical changes caused by irradiation of polymer with ultraviolet or visible light" (Schnabel, 1981, p. 14)

Parylene: the generic name for a series of poly-paraxylylene polymers, both substituted and nonsubstituted varieties, except when used in reference to conservation studies, where **parylene** refers to the parylene N and parylene C only.

parylene C: the chlorinated variation of parylene polymer, also known by the chemical name 'polychloro-p-xylylene'.

parylene N: the nonsubstituted variation of the parylene polymer, also known by the chemical name 'poly-paraxylylene'

Silk: refers to the fibroin protein fibres extruded by the *Bombyx mori* moth larvae, with the sericin gum removed.

CHAPTER 2 REVIEW OF THE LITERATURE

Introduction

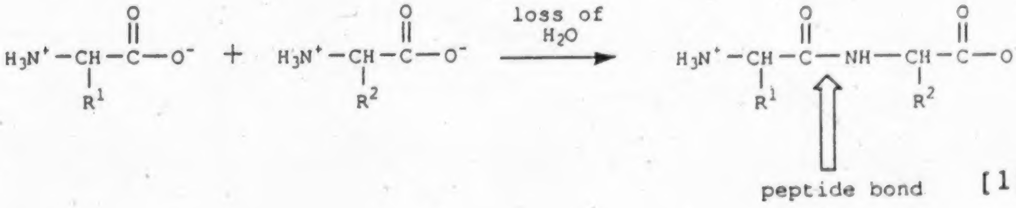
In order to preserve silk artifacts, many of which are unique and of historic value, it is necessary to have an understanding of the factors involved in the degradation of this fibre, and a familiarity with various methods of measuring degradation. The following literature review begins by summarizing silk fibre structure, morphology, and properties. The causes and measurement of silk degradation are then addressed. The polymerization process, properties and uses of the parylene polymer coating will then be discussed.

Silk

Structure of Proteins

Proteins are natural polymers which are characterized by the specific amino acids from which they are built. Each of these α-amino acid units contains a side chain (R), an amino group and a carboxyl group. The side chain, which can be neutral, basic, or acidic, small or bulky, is instrumental in determining the physical and chemical properties of the resultant protein.

The positively charged amino group and the negatively charged carboxyl group give rise to a zwitterionic, or dipolar structure. Amide bonds are formed through a condensation reaction between the amino and carboxyl groups of adjacent residues, as shown:



$$H_3N^+-\underset{R^1}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^- + H_3N^+-\underset{R^2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^- \xrightarrow{\text{loss of } H_2O} H_3N^+-\underset{R^1}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-NH-\underset{R^2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^-$$

[1]

These amide links between amino acid residues are called peptide bonds. Polymers formed in this manner are called peptides; proteins are peptides with molecular weights from approximately 6000 to 40,000,000 (Wade, 1987).

Proteins can be classified as either globular or fibrous. Globular protein molecules, such as haemoglobin and insulin, form coils and are roughly spherical in shape. Fibrous protein chains are extended and are usually insoluble in water. Wool and silk are examples of fibrous proteins.

Structure of Silk

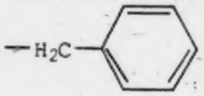
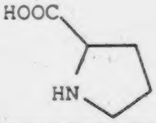
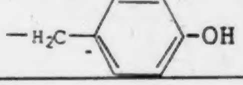
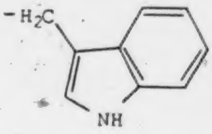
Raw silk is composed of two types of protein, fibroin and sericin. The pairs of filaments, or brins, extruded by the *Bombyx mori* moth larvae are made from fibroin, and are bound together by gum-like sericin (Otterburn, 1977).

Fibroin Chemical Composition

Fibroin contains approximately 16 α-amino acids which are listed in Table 1. Most frequently occurring are the small and simple residues glycine, alanine and serine, which together account for 80% to 85% of all the residues in the protein (Robson, 1985). The number of acidic residues (glutamic and aspartic acid) is low, as is the number of basic residues (lysine, histidine and arginine). The majority of polar amino acids are serine, threonine and tyrosine, all of which contain hydroxyl groups (Otterburn, 1977). A very small amount of cystine (0.23%) is also present (Lucas, 1966).

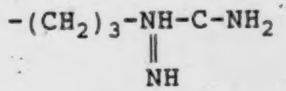
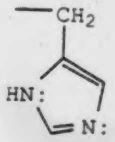
The molecular weight of fibroin is still uncertain. Estimates have ranged from 33,000 daltons using osmotic pressure determination (cited in Otterburn, 1977, p.58) to 1,000,000 (Mercer, 1954) using light scattering measurements. Some more recent studies employing solubilization of gland fibroin extracts using urea or guanidine-HCl have given more consistent values, from 350 000 (Sprague, 1975) to 370 000 (Tashiro, Otsuki, & Shimadzu, 1972).

Table 1
Amino Acid Composition of *Bombyx mori* Fibroin

Amino Acid	N[a]	R[b]	Side Chain Structure
	Side Chain is Neutral		
Glycine (Gly)	43.74	445	-H
Alanine (Ala)	28.78	293	$-CH_3$
Valine (Val)	2.16	22	$-CH(CH_3)_2$
Leucine (Leu)	0.52	5	$-CH_2CH(CH_3)_2$
Isoleucine (Ile)	0.65	7	$-CH(CH_3)CH_2CH_3$
Phenylalanine (Phe)	0.62	6	
Proline (Pro)	0.35	3	
	Side Chain Contains a Hydroxyl Group		
Serine (Ser)	11.88	121	$-CH_2OH$
Threonine (Thr)	0.89	9	$-CH(OH)CH_3$
Tyrosine (Tyr)	5.07	52	
	Side Chain Contains a Non-Basic Nitrogen		
Tryptophan (Trp)	0.33	2	

Continued

Table 1 (Continued)
Amino Acid Composition of *Bombyx mori* Fibroin

Amino Acid	N[a]	R[b]	Side Chain Structure
Side Chain is Acidic			
Aspartic Acid (Asp)	1.28	13	$-CH_2COOH$
Glutamic Acid (Glu)	1.00	10	$-CH_2CH_2COOH$
Side Chain is Basic			
Lysine (Lys)	0.63	3	$-(CH_2)_4-NH_2$
Arginine (Arg)	1.83	5	 $-(CH_2)_3-NH-\underset{\underset{NH}{\|}}{C}-NH_2$
Histidine (His)	0.53	2	
Side Chain Contains Sulfur			
Cystine (Cys) (half)	0.15	2	$-CH_2-SH$
Methionine (Met)	0.07	1	$-CH_2CH_2-S-CH_3$

Note. Adapted from Lucas and Rudall, 1968, p. 484; Wade, 1987, p. 1218-1219.
[a] amino acid nitrogen as % of total nitrogen.
[b] Number of amino acid residues per 1000 residues estimated.

Fibroin Structure

Primary structure.

The primary structure is the covalently bonded structure of the protein molecule, and refers to the sequence in which the amino acid residues are combined (Wade, 1987). The precise sequence of amino acids in silk has yet to be determined. The residues at the N-terminus (the end of the protein terminating in an amino group) are glycine, alanine, and serine (Truter, 1973). Glycine, alanine, serine, as well as tyrosine, valine and proline (Shaw & Smith, 1954) have all been postulated for the C-terminus residues.

Because several different terminal residues have been isolated, it is possible fibroin has a multi-chain primary structure composed of several polypeptides linked by inter-chain bonds (Shaw, 1964). Research by Sprague (1975) concluded the protein was made up of equal amounts of two distinct polypeptides, each of which appeared to contain the same proportions of the major amino acids (glycine, alanine and serine). Sasaki and Noda (1973) proposed that fibroin is made from one long and three short polypeptides linked by disulphide bonds. Disulphide bonds between chains are theoretically possible because fibroin contains a small amount of cystine (Shaw, 1964), but Otterburn (1977) states there is no direct evidence of cystine forming these bonds between the polymer chains. Ester linkages have also been suggested by Zuber (cited in Robson, 1985, p. 682).

In order to determine its sequence of amino acids, the fibroin must be broken into smaller segments and the composition of these analyzed. The sequence of the fragments must then be found. Partial acid hydrolysis breaks the chain in a random manner. Using this technique, the following minimum repeating unit for fibroin was suggested by Levy and Slobodian (1952):

X-Ala-Gly-Ala-Gly-Y [2]

where X and Y are residues other than alanine and glycine. The use of enzymes rather than acids for hydrolysis is a more selective technique, causing breakage at known points along the chain (Wade, 1987). Lucas, Shaw and Smith (1957) digested fibroin with chymotrypsin, which cleaves the chain at the carboxyl group of the tyrosine, phenylalanine and tryptophan residues (Wade, 1987). A solution (Cs) and a precipitate (Cp) were obtained. An analysis of Cp, which accounted for 60% of the fibroin's total nitrogen, yielded the following structure:

$$\text{Gly-Ala-Gly-Ala-Gly-[Ser-Gly-(Ala-Gly)}_n]_8\text{-Ser-Gly-Ala-Ala-Gly-Tyr} \quad [3]$$

where n usually equals 2. Similar structures were confirmed by Fraser, Macrae and Stewart (1966). Drucker, Hainsworth and Smith, (1953) found the X-ray pattern given by Cp was identical to that of the original fibroin, but indicated a higher crystallinity. They concluded the Cp portion represented the crystalline regions of the unbroken molecule.

The remaining 40% of the fibroin contained in the solution (Cs) was also studied, but many questions remain. The different polypeptides found by several researchers are listed by Otterburn (1977) and Robson (1985). The predominant peptides shown as structures 4, 5, and 6 were those isolated by Lucas, Shaw and Smith (1962). These three peptides make up about 75% of the Cs fibroin residues.

Gly-Ala-Gly-Ala-Gly-Ala-Gly-Tyr [4]
$\text{Gly-(Gly}_3\text{-Ala}_2\text{-Val)-Tyr}$ [5]
Gly-Ala-Gly-Tyr [6]

Other studies have employed the use of the trypsin enzyme to cause cleavage at the carboxyl group of lysine and arginine residues (Wade, 1987). The results of such a study by Shaw (1964) combined with the results from the chymotrypsin studies led Shaw to propose a three phase primary structure for fibroin. Phase I is composed of the Cp sequence corresponding to the crystalline regions of the molecule (60%). Phase II, 30%, contains sequences of glycine, alanine, valine and tyrosine. Phase III, contains the remaining 10% of the residues, including those with acidic, or bulky side chains. How these phases are related to the multi-chain structure of fibroin is not certain. Each polypeptide may be a combination of phases, or limited to one phase (Shaw, 1964). Many of the fibre's properties are dictated by the fact that fibroin is composed of 80% to 85% glycine, alanine and serine, all of which lack bulky side chains.

Secondary structure.

Individual protein molecules tend to be held by hydrogen bonds in coiled (α-helix) or folded (ß-pleated sheet) structures. This orderly arrangement is called the secondary structure (Wade, 1987).

Through X-ray diffraction techniques, silk fibroin has been found to have a ß-pleated sheet structure. According to Meyer and Mark (cited in Robson, 1985, p.667), extended protein chains parallel to the fibre axis are linked by hydrogen bonds between carbonyl and amino groups on adjacent chains. Because silk is composed primarily of residues which lack bulky side groups, the fibroin molecules can pack closely together allowing hydrogen bonding to occur, thus producing a highly crystalline fibre (Peters, 1963).

Tertiary structure.

The way by which the protein chain forms 3-dimensional arrangements is called the tertiary structure (Wade 1987). The tertiary structure includes both ordered, crystalline regions, and regions of disorder.

The three phase model postulated by Shaw (1964) can also be applied to the tertiary structure. Phase I forms a crystalline ß-structure (pleated sheets). Phase II is not as well ordered, but is not entirely amorphous, and Phase III, with its bulky side chains, constitutes the amorphous regions (Shaw, 1964). Drucker et al. (1953) and Peters (1963) also relegated larger residues to amorphous regions. However, Marsh, Corey, and Pauling (1955) stated these bulkier residues may be incorporated within the crystalline areas, causing deformations in the crystal structure. Robson (1985) also warns against the assumption that bulky groups occur exclusively in amorphous areas.

Marsh et al. (1955) and Warwicker (1960) have postulated a three dimensional antiparallel ß-structure as the crystalline tertiary structure. Extended chains of amino acids, with glycine alternating with the larger alanine or serine residues, are hydrogen bonded laterally to form pleated sheets. These sheets are then stacked in an antiparallel manner, meaning the sheets are stacked back to back; the glycine side chains from one sheet lie next to the glycine chains of the adjacent sheet (Figure 1). In this manner, 3-dimensional crystalline regions are formed. Lim and Steinberg (1981) proposed an entirely different tertiary structure, consisting of several fibroin proteins forming a parallel-chain, tape-like structure, which then coils into a flat helix.

Fine structure.

A fibre's fine structure "is a complex combination of long-chain molecules in crystalline and non-crystalline regions, which may in turn be aggregated into fibrils or other supra-molecular structures" (Hearle, 1963a, p.209). As previously mentioned, silk is approximately 60% crystalline, the remaining 40% being more random in arrangement and likely containing the bulkier residues. The crystalline regions are oriented parallel to the fibre axis, whereas chains in the amorphous regions are more randomly arranged (Robson, 1985).

Electron microscopy has shown the fine structure of silk to consist of ribbon-like filaments, or microfibrils lying parallel to the fibre axis (Dobb, Fraser, & Macrae, 1967;

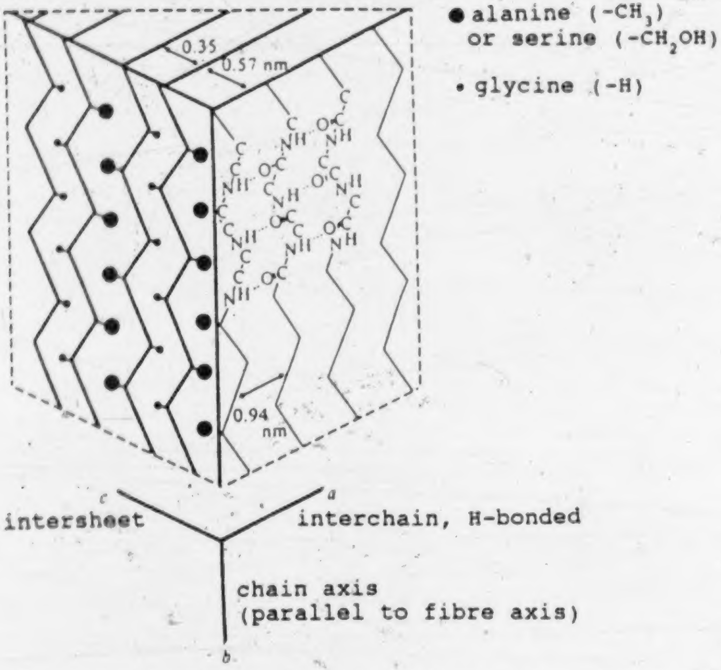

● alanine (-CH_3)
or serine (-CH_2OH)
• glycine (-H)
0.35
0.57 nm
0.94 nm
C
NH
O
c
intersheet
a
interchain, H-bonded
chain axis
(parallel to fibre axis)
b

Figure 1. The antiparallel ß-pleated tertiary structure of *Bombyx mori* silk fibroin.

Note. From "Silks- Their Properties and Functions" by M. W. Denny, 1980, *Symposia of the Society for Experimental Biology, 34*, p. 258. After Marsh et. al, 1955, "An Investigation of Silk Fibroin", 1955, *Biochimica et Biophysica Acta, 16*, p. 13-18. Reprinted by permission.

Marsh et al, 1955). Dobb et al. (1967) proposed that microfibrils are composed of the crystalline ß-structure portion of fibroin such that the pleated sheets lie parallel to the longer, lateral dimension of the microfibril. The amorphous regions of the fibre occupy the space between the microfibrils. Some doubt, however, has been cast on Dobb et al.'s findings, due to possible cellulose contamination (Millward, 1969).

Summary.

In summary, silk fibroin comprises mainly the simple amino acids alanine, glycine, and serine. A primary structure consisting of a multi-chain arrangement of polypeptide chains has been proposed. The fibroin chains form pleated sheets as a secondary structure, which then stack to produce a ß-antiparallel tertiary structure in crystalline regions. The crystalline areas may then combine together to form ribbon-like microfibrils which make up the fibre's fine structure.

Sericin

When extruded by the *Bombyx mori* larvae, the pairs of fibroin filaments, are cemented together by a second protein present in raw silk, sericin. This protein is significantly different in chemical composition from fibroin, with serine, glycine and aspartic acid residues making up two thirds of its content (Robson, 1985). During the processing of silk for textile usage, the sericin is removed by soaking in a hot dilute soap or alkaline solution, in a process called degumming. The removal of the gum improves the softness and lustre of the silk fibres (Peters, 1963).

Properties of Silk

Morphology

Before degumming, the silk cross-section consists of two roughly triangular filaments which together form an elliptical shape. After degumming the triangular filaments, called brins, separate and appear smooth and translucent in the longitudinal direction, with few external markings (Peters, 1963).

Fibre diameter for brins varies from approximately 7 μm to 12 μm depending on spinning conditions and the location within the cocoon (Robson, 1985).

Physical Properties

The physical properties of silk, using typical values, are summarized in Table 2. Of all the natural fibres, silk is the most similar to synthetic fibres because of its reasonably high strength and breaking extension, which result in a high work of rupture (Robson, 1985). These properties can be explained by examining changes which occur on the molecular level. The silk fibre is made up of oriented crystalline

Table 2
Properties of Silk Fibres

Property	Typical Value	Source
Density	1.33g/cm^3	The Textile Institute, 1975, 134
Refractive Index	$n\| = 1.591$	The Textile Institute, 1975, 133
	$n^{\perp} = 1.538$	
Birefringence	n= 0.053	The Textile Institute, 1975, 133
Tenacity	0.38 N/tex	Meredith, 1945, T127
Wet Strength (% of dry strength)	75% to 85%	Cook, 1968, 159
Initial Modulus	7.3 N/tex	Meredith, 1945, T127
Work of Rupture	59.7 mN/tex	Meredith, 1945, T127
Breaking Extension	23.4%	Meredith, 1945, T127
Elastic Recovery (2% extension)	92%	Harris, 1954, 109
Moisture Regain	9.9% absorption 11.05 desorption	Hutton & Gartside, 1949, T167
Swelling in Water (% increase in cross-sectional area)	30% to 41%	Harris, 1954, 201

regions, and randomly oriented amorphous areas. The molecules are held together by hydrogen and ionic bonds and Van der Waals forces. A single molecule can pass through both crystalline and amorphous regions (Robson, 1985).

When a load is applied, the amorphous areas are the first to become deformed. Silk has a relatively high resistance to deformation, or initial modulus, because of the strong forces between chains in the amorphous regions, and the strong interaction between amorphous and crystalline regions (Robson, 1985). Elastic recovery is complete if no bonds are broken. If more tension is applied, inter-chain bonds begin to break in the amorphous regions, allowing the molecules to slide past one another and become extended in a process called 'plastic flow'. Permanent deformation occurs when bonds are formed between the newly extended chains. When the chains in the amorphous regions are fully extended, the load is then transferred to the already oriented, extended crystalline regions. When the load can no longer be accommodated, breakage of hydrogen bonds in the crystalline regions occurs, and peptide bonds may also be broken, resulting in fibre rupture (Robson, 1985).

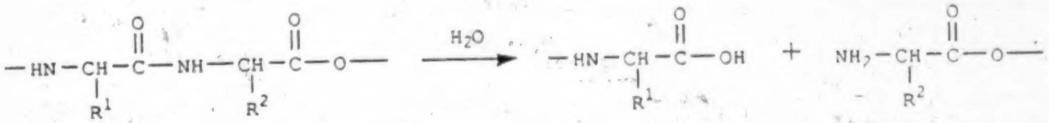
The elastic recovery of silk is affected by both the fineness of the fibre and by moisture content. Moisture also affects other physical properties. Water molecules enter the fibre in the amorphous regions, and compete for the hydrogen-bonding sites between the chains. The result is a general loosening of the structure which allows the amorphous chains to slide past each other more easily, causing greater extensibility and decreased modulus and strength (Denny, 1980; Lucas et al, 1955).

Chemical Properties

Silk fibroin can undergo several types of chemical reactions including hydrolysis, oxidation, and cross-linking. The mechanisms for these reactions, and how their effects can be measured, are outlined below. The action of specific acids, alkalis and other chemicals, as well as the effect of light and heat will be discussed in the subsequent section on degradation.

Hydrolytic effects.

The fibroin protein can undergo hydrolysis, during which a molecule of water is added across the peptide linkage. This causes breakage of the main protein chain as shown:



$$-HN-\underset{R^1}{CH}-\overset{O}{\overset{\|}{C}}-NH-\underset{R^2}{CH}-\overset{O}{\overset{\|}{C}}-O- \xrightarrow{H_2O} -HN-\underset{R^1}{CH}-\overset{O}{\overset{\|}{C}}-OH + NH_2-\underset{R^2}{CH}-\overset{O}{\overset{\|}{C}}-O-$$

[7]

Exposure to acids will cause cleavage in a random manner along the polymer, whereas damage from alkalies appears to occur initially at the polymer ends (Otterburn, 1973; Peters 1963).

The extent to which hydrolysis occurs depends upon the pH of the hydrolytic agent, with the least damage generally caused by reagents having a pH between 4 and 8. The damage is most severe when silk is exposed to reagents above pH 11 and below pH 3 (Harris, 1943).

Hydrolytic damage is shown by a decrease in tensile strength as revealed through physical testing, and through several chemical tests. A fluidity measure of a fibroin solution in cupri-ethylene-diamine indicates the degree of degradation. The solution of a more broken-down polymer, consisting of shorter chains, will have a higher fluidity. Another chemical means of assessing hydrolytic damage is to measure the amount of amino nitrogen. As shown in equation 7, when a peptide link is hydrolysed, the chain is broken to form an amino group and a carboxyl group. The increase in amino groups, or amino nitrogen content, can then be used as a measure of hydrolytic degradation. Generally, chemical tests for degradation are believed to be more sensitive than physical, and can detect smaller amounts of damage before they are manifested in physical change (Burgess & Hanlan, 1980).

Oxidative effects.

Oxidative reactions introduce oxygen-containing groups along the polymer chain. The oxidation reactions undergone by silk are very complex, and are thought to affect the polymer in three ways: oxidation of the tyrosine side chains, oxidation of the N-terminal residues, and breakage of the polypeptide links in the polymer backbone (Otterburn, 1973; Peters, 1963; Robson, 1985).

Autoxidation, which occurs through a free radical chain mechanism, can cause great damage to polymers due to the self-perpetuating nature of these reactions (Schnabel, 1981). Autoxidation proceeds through three steps: initiation, propagation and termination.

Initiation involves the production of highly reactive free radicals. Heat, light and chemical factors can all initiate autoxidation of a polymer (P):

$$P \xrightarrow{h\nu\ \Delta} P\cdot + P\cdot \qquad [8]$$

During the propagation steps, the free radical (P·) reacts with oxygen to form peroxy polymer radicals by addition:

$$P\cdot + O_2 \rightarrow P\text{-}O\text{-}O\cdot \qquad [9]$$

The peroxy radical then abstracts a hydrogen, either from a neighbouring polymer chain or intramolecularly to form a polymer hydroperoxide (POOH):

$$P\text{-}O\text{-}O\cdot + P\text{-}H \rightarrow P\text{-}O\text{-}O\text{-}H + P\cdot \qquad [10]$$

The new radical produced can then react further to continue the chain reaction until termination is reached. The polymer hydroperoxide, upon exposure to light, can decompose to form highly reactive polymer oxy radicals (PO·) and hydroxy radicals (OH·),

$$P\text{-}O\text{-}O\text{-}H \rightarrow P\text{-}O\cdot + \cdot O\text{-}H \qquad [11]$$

which can then abstract a hydrogen from the same, or neighbouring polymer chains:

$$PO\cdot + PH \rightarrow POH + P\cdot \qquad [12]$$
$$HO\cdot + PH \rightarrow P\cdot + H_2O \qquad [13]$$

Polymer oxy radicals can also participate in other reactions leading to chain scission and the formation of in-chain ketone groups (Rabek, 1990).

According to Rabek (1990), termination most often occurs when two radicals combine to create inactive products:

$$\left.\begin{array}{l} P{-}O{-}O\cdot + P{-}O{-}O\cdot \rightarrow \\ P{-}O{-}O\cdot + P\cdot \rightarrow \\ P\cdot + P\cdot \rightarrow \end{array}\right\} \text{non-radical products} \qquad [14]$$

When silk is oxidized a change in colour varying from yellow, to pink, to brown is observed (Otterburn, 1973; Peters, 1963). Some researchers have proposed that the oxidation of tyrosine residues may produce coloured o-quinones; however, the presence of these products has not actually been detected (Sitch & Smith, 1957). In addition to colour change, oxidation causes a deterioration of physical properties, and a decrease in molecular weight (Kamiya & Niki, 1978).

Oxidative damage can be assessed by the methylene blue absorption test, as was employed by Stitch and Smith (1957). This test measures the degree to which the phenolic tyrosine residue has been oxidized to form an acidic product. The more of the basic blue dye absorbed, the greater the oxidative damage.

When silk is oxidized, ammonia is produced. The amount of ammonia nitrogen present can then be used as a measure of oxidative damage. Fluidity measures as used for hydrolytic detection may also be used to indicate the extent of peptide breakage through oxidation.

Cross-linking effects.

By exposing silk to various cross-linking agents, covalent bonds can be formed between chains. This technique has been employed for structural studies of silk as well as in attempts to alter properties. For example, Oku and Shimizu found cross-linking with formaldehyde caused silk to swell in water, and helped to reduce water-spotting problems (cited in Robson, 1985, p. 687).

Degradation of Silk

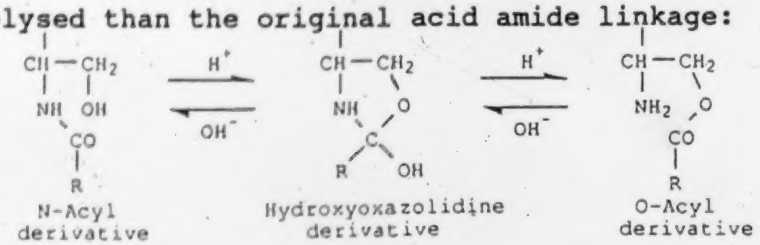
Causes of Degradation

Factors which contribute to the breakdown of silk include chemical damage, and damage through exposure to light and heat. Each of these factors will be discussed briefly below.

Chemical degradation.

Studies focusing on the chemical reactivity of silk are usually done by industry, and therefore focus on chemical reactions that occur during the processing of silk (Miller, 1986; Otterburn, 1977).

Acids are easily absorbed by silk fibres and once absorbed, are difficult to remove (Cook, 1968). Hydrolysis occurs upon exposure to mineral acids and alkali, with exposure to mineral acids generally being most damaging. Hot concentrated hydrochloric acid will readily dissolve silk and is often used in hydrolytic studies (Peters 1963; Otterburn, 1985). Sulphuric acid can also cause sulphonation of tyrosine residues, and with extended exposure, may cause an N→O peptidyl shift to occur (Iwai & Ando, 1967). The resulting O-acyl product has an ester linkage which is more easily hydrolysed than the original acid amide linkage:



[15]

Exposure to sulphuric acid also causes fabrics to shrink, and a loss of lustre is observed (Guoping & Slater, 1990). Nitric acid not only causes degradation through hydrolysis of peptide bonds, but also causes nitration of residues containing benzene rings, resulting in a yellowing of the fibre (Otterburn, 1977; Peters, 1963; Robson, 1985).

Silk shows good resistance to dilute organic acids at room temperature (Howitt, 1946). Low concentrations of tartaric and citric acids are occasionally used in processing to produce a rustling effect called 'scroop', without causing damage. Some concentrated organic acids (98% formic acid) can cause degradation (Robson, 1985). In moderate concentrations, acid causes silk fibres to contract, an effect used in producing crepe fabrics (Cook, 1968).

Silks exposed to alkali become stiff and have a tendency to split into fibrils. This breakdown of physical structure is followed by hydrolysis of peptide bonds (Tweedie, 1938). Whereas acid-induced hydrolysis causes chain scission randomly along the polymer length, alkali attack appears to concentrate at the polymer ends (Lucas, Shaw & Smith, 1958). A treatment with hot alkali also causes a loss of about one third of both the hydroxyamino acids serine and threonine residues and an increase in amide nitrogen (Peters, 1963; Nicolet & Shinn, 1941).

Several studies have also proposed that alkalies can produce cross-linking between residues. Robson and Zaidi (1967) claimed exposure to alkali (K_2CO_3) caused cross linkages to form between serine and lysine residues.

Prolonged exposure to boiling water and steam is used in the degumming process can cause hydrolysis, but at a slow rate (Otterburn, 1977; Robson, 1985). Fibrous silk is also highly resistant to enzymic hydrolysis due to its highly crystalline structure. In order to be broken down by enzyme action, the fibre must first be swollen and dissolved in a solvent (Otterburn 1977; Peters, 1963; Robson, 1985).

Hydrogen peroxide and peracids are used to bleach pigmented silks, and are capable of causing damage through oxidation (Robson, 1985). Sitch and Smith (1957) concluded that treatment with hydrogen peroxide or peracid caused cleavage of the tyrosine residue and the tyrosine oxidized to form an acidic product. More acidic groups were formed, and chain breakage was more rapid using peracetic acid than hydrogen peroxide. Oxidation by potassium permanganate was seen by Earland and Stell (1957), and Earland, Stell and Wiseman (1960) to form cross links between tyrosine residues. These linkages were thought to be responsible for the insolubility of fibroin oxidized in this manner.

Silk fibres also have a strong affinity for salts (Cook, 1968) which explains the tendering and staining caused by perspiration on silk clothing. The damaging effect produced by chlorides is thought to be connected to the presence of iron, copper, and other chemicals used to enhance the rustling 'scroop' effect of silk fabrics, and is likely oxidative in nature (Howitt, 1946). Peters (1968) states that chlorine causes oxidative damage through attack on tyrosine residues.

Miller (1986) exposed new silk fibres and fabrics to a variety of chemicals. The effects of acid, alkali, peroxide, and boiling water were all studied. The chemicals chosen were those used in the processing and dyeing of silk. These included sulphuric acid (0.5N), sodium hydroxide (0.5N, 0.75N, 1.0N) and hydrogen peroxide (1N, 10N). She concluded these simulations of silk processing produced a statistically significant ($p>0.05$) reduction in tenacity, elongation and intrinsic viscosity, and that each treatment caused changes in the amounts of two or more amino acids.

Thermal degradation.

Exposure to high temperatures causes irreversible damage to silk fibroin. Magosi and Nakamura (1975) reported silk to have a glass transition temperature of 175 °C, crystallization temperature of 212 °C, and a decomposition temperature of

280 °C. According to the wet heat studies done by Hagiwara and Kato (cited in Miller, 1986, p. 23), at 100 °C NH_3 is given off, but the fibroin does not visually appear to decompose. Some degradation was seen to occur at 125 °C, and increased at temperatures over 150 °C. The breakage of hydrogen bonds, and subsequent disorientation and hydrolysis of the molecular chains was said to have occurred, as well as an additional competing reaction resulting in increased crystallinity.

The exposure of a polymer to thermal energy causes increased vibration of intramolecular bonds until their bond dissociation energies are exceeded, causing them to break. This type of damage is not common at lower temperatures (150°-300° C), but those breakages that do occur can initiate autoxidation reactions through the formation of a peroxide radical (Schnabel, 1981), as was demonstrated by equations 8 to 13 in the previous section on oxidation. Miller (1986) studied thermal degradation of silk in the presence and absence of air. Some samples were heated in ambient air and others in a vacuum for 8 hours at 125 °C. Those samples heated in a vacuum did not exhibit a statistically significant loss in strength, elongation, or viscosity, while those exposed to air under the same conditions showed a 7% loss in strength.

Hansen and Ginell (1989) exposed silk to dry temperatures of 70°, 80°, 90°, 110° and 150 °C for 158, 109, 118, 45 and 7 days respectively. The rate of deterioration for tensile properties increased with the higher temperatures. The effect of dry heat on silk was also investigated by Hersh, Tucker and Becker (1989). During 96 hours of exposure to a temperature of 150 °C, breaking strength was found to decrease in a linear manner, the overall strength being reduced to 30% of the original.

Hersh, Tucker, and Becker (1989) also observed a dramatic yellowing of the silk; the CIElab* system of colour measurement indicated an overall colour change of 39.39 units. A visible yellowing of silk occurred after only 6 hours of exposure. Yellowing was seen to be less pronounced at lower temperatures by Hansen and Ginell (1989). Even after 130 days at 70° C, the total colour change (ΔE) was less than 5 units. Kuruppillai, Hersh and Tucker (1986) noted that dry heat degradation followed first order property kinetics. This allows "the extent of degradation to be calculated for any heating or exposure times on the basis of measurements made after only a few different heating times" (p.125).

The effect of humidity on thermal degradation rate was considered by Hansen and Ginell (1989) using a Hot Pack Temperature-Humidity Chamber. Samples were exposed to relative humidities of <5%, 50%, 70% or 90% ± 2, at a temperature of 90 °C for 17 days. The degradation rate increased rapidly above a relative humidity of 50%, with very little change in properties evident between 0% and 50%. Setoyama (1982/1983) also found silk samples heated in sealed tubes yellowed more when temperature and moisture content were increased.

Bresee and Goodyear (1986) studied the types of fibre fractures found in historic silk and silk aged by heat and light. By analyzing the frequencies of the types of fractures produced, they concluded laboratory heating (for 6 hours at 60±2 °C) resulted in increased embrittlement and loss of interfibrillar cohesion.

Researchers have tested the effect of deacidifying agents and antioxidants on the rate of silk degradation. The retardants examined by Kuruppillai et al. (1986) were seen to have little effect on improving breaking strength after exposure to heat, but did appear to retard the formation of amino groups.

Photochemical degradation.

Damage to textiles by light is of two types, photolysis and photosensitization. In order for the absorbed light to cause degradation, it must be of the correct wave-length to excite or energize the fibre molecules, such that they become chemically reactive. When bonds are directly broken by light energy, photolysis has occurred (Tucker, Kerr, & Hersh, 1980). This type of damage is caused by short-wave UV radiation. Light induced autoxidation can occur when a molecule absorbs a photon of light energy producing an excited state(*) (Schnabel, 1981).

$$M + h\nu \rightarrow M^* \qquad [16]$$

The excited molecule can then lose this absorbed energy through fluorescence, phosphorescence, internal conversions (heat), or photochemical reaction. In order for a photochemical reaction to occur, the molecule is usually in an excited triplet state which has a longer lifetime than a singlet state (Zollinger, 1987).

The excited molecule may then dissociate to form free radicals ($R_1\cdot$ and $R_2\cdot$) which are capable of propagating a free radical chain reaction with oxygen (Schnabel, 1981).

$$M^* \rightarrow R_1\cdot + R_2\cdot \qquad [17]$$

Most polymers do not absorb radiation having wave-lengths longer than 300 nm (Kamiya & Niki, 1978; Schnabel, 1981). Because radiation with wave-lengths less than 340 nm is filtered out by the atmosphere and by glass, photosensitization is more commonly a problem. For photosensitization to occur, a second substance which is chromophoric and thus is capable of absorbing near UV or visible light, such as a dye, is necessary. Kelly, Mollah and Wilkinson (1990) suggest two or more amino acid side chains may act together as a chromophoric group. They also propose naturally occurring impurities which are not removed by solvent extraction may also be involved.

The energy absorbed by the chromophores is transferred to the textile (Miller, 1986; Tucker et al, 1980). The following mechanism for this transferal was proposed by Egerton (1948b): The light energy absorbed by the dye is transferred to surrounding air, activating the oxygen which can then combine with water vapour to form hydrogen peroxide. The fibres can be attacked either by the activated oxygen itself, or by the hydrogen peroxide.

To study changes in silk fibroin structure by UV radiation, Tsukada and Hirabayashi (1980) used a 10 watt incandescent ultraviolet bulb with a main wavelength of 253.7 nm. The degummed filaments were placed 20 cm under the bulb and kept at a temperature of 25 °C and 65% humidity for 10 to 45 hours. Using birefingence and X-ray studies, the researchers concluded the degree of orientation for fibroin decreased slightly with exposure to UV light, while the degree of crystallinity remained the same. Strength and elongation sharply decreased within the first 10 hours of exposure. This damage could be due to photolysis due to the purity of the fibres tested, and the low wavelength used to irradiate the samples.

Egerton's study (1948a) on the effects of light on fluidity and tensile strength changes of vat dyed rayon, silk, and nylon was concerned with degradation due to photosensitization. Dyed silk yarns were exposed to sunlight in a south-facing sun gallery for 1000 microwatt-hours/cm^2 /10 Å, and 4000 microwatt-hour/cm^2/10 Å, measured using a photographic recorder. Results showed the presence of yellow and orange coloured anthroquinone and indigoid dyes greatly accelerated loss in tensile strength of the fabric, and that the effect was enhanced by high humidity.

There is further evidence that the damage done to silk by light is oxidative in nature. Harris (1934) placed silk yarns in a vacuum, and in atmospheres of hydrogen and oxygen, exposing them to north skylight for 4 months. Those in the vacuum and hydrogen atmosphere retained their strength, while strength loss was apparent in oxygen-exposed samples. Egerton (1948a) irradiated undyed yarns with a 250 watt mercury vapour lamp in the presence of different atmospheres. Virtually no strength loss occurred for those samples exposed to carbon dioxide or nitrogen, whereas those exposed to air or pure oxygen exhibited strength loss of 31% to 55%.

Work by Okamato (cited in Lucas et al., 1958, p. 189; Robson, 1985, p. 688) showed tyrosine, threonine and leucine as the residues most affected by photodegradation, and that damage was most rapid in the amorphous regions. Nakanishi and Kobayashi, (cited in Lucas et al., 1958, p. 189; Robson, 1985, p. 689) postulated degradation occurs first by the breaking of hydrogen bonds, followed by oxidation of the tyrosine residues, and eventual chain scission at the tyrosine residue. Their results indicated fibroin is oxidized by light, while simultaneously being hydrolysed by water.

The effect of humidity on the photodegradation of silk fibroin has been investigated. Undyed yarns were enclosed in cells containing 0% and 100% relative humidity, and were placed in a south-facing sun gallery for 6 months. The sample exposed to high humidity exhibited a 100% loss in strength, whereas the dry sample showed a 65% loss (Egerton, 1948a).

The effect of pH on photodegradation of fibroin was studied by Harris (1934). Samples treated with 0.1N NaOH and 0.1N H_2SO_4 were exposed for up to 175 days to sunlight, under glass. Those samples treated with acid had a higher strength loss than the alkaline samples.

In addition to deterioration of tensile properties, silk also yellows during photodegradation, possibly due to degradation of tryptophan residues (Okamoto & Kimura, 1954). The results of Holt, Milligan and Savige (1977) indicated that tryptophan was responsible for some yellowing of bleached or fluorescently whitened wool, but had less support for its effect on unbleached, unwhitened wool. Photodecomposition of histidine or tyrosine residues (Inglis & Lennox, 1963) or the introduction of double bonds (Hoare, 1974) have also been suggested as contributing to the photoyellowing of wool, so may also play a role in silk (Holt et al., 1977).

Weighting agents.

The presence of weighting agents in silk is known to increase the fibre's sensitivity to degradation. By the late 19th century, the addition of these compounds was a standard procedure in the processing of silk.

The weighting process was originally adopted in order to replace the weight lost during degumming, and allowed the weight of the silk to be increased 30% to 300%. By treating the silk with the inorganic salts of aluminum, iron, lead, tin, or zinc, the hand, body, "scroop" and drape of the fabric were improved (Becker, Hersh, & Tucker, 1987).

Tin salts are the most frequently used weighting agent. The fibres are treated with anhydrous stannic chloride which is then hydrolysed to form an insoluble salt within the fibre. This salt is then exposed to sodium phosphate to form high molecular weight complexes. This process is repeated several times to further increase the weight. The silk is then boiled in sodium silicate to produce a high molecular weight, insoluble tin silicophosphate. The appearance of the silk is not noticeably changed because the salts are deposited within the fibre (Robson, 1985).

Weighting agents are often responsible for deterioration of physical properties caused by acid hydrolysis and oxidation during exposure to light, storage, or from the weighting process itself (Robson, 1985). Upon exposure to light, weighted silk may degrade more quickly than nonweighted because most weighting agents are highly acidic (Becker et al., 1987). Harris (1934) showed silk with an acidic pH to be very unstable to light. The effect of humidity on the degradation of weighted silk was found to be small, indicating the photosensitizing reaction occurs through the formation of an activated oxygen intermediate rather than through a hydrogen peroxide intermediate (Egerton, 1948b).

Weighted silk samples exposed to 4 months of natural sunlight through glass were found to have a higher loss of tensile strength than those stored in the dark (Roberts and Mack, 1936). D'Olier and Mack (1936) also showed strength loss to occur after 6 months, and 23 months of storage in darkness.

In the study by Roberts and Mack (1936), samples were given repeated passes through tin chloride and disodium phosphate baths, and strength per thread was compared to an unweighted control. Results showed a considerable loss of strength occurred due to the weighting process itself, and that strength decreased with increased number of treatments.

Summary and Comparison of Degradative Forces

Exposure to chemicals, heat, or light affect silk fibroin in different ways. Miller (1986) found exposure to xenon arc lighting, and sodium hydroxide treatments had the greatest effect on tenacity and elongation. Heat in the presence of air, exposure to light, and chemical treatments all produced statistically significant ($p<0.05$) changes in the proportions of at least two amino acids. In general, the amino acids with bulky side chains were most affected. Because these residues are most likely found in noncrystalline regions of the fibre, Miller's results suggest the attack occurred primarily in the amorphous areas.

Bresee and Goodyear (1986) used SEM to discover differences in the type of fibre fracture most frequently found in silks aged by different means. Brittle fractures were frequent in samples aged by heat, whereas surface-flaw fractures were dominant for light aged fibres. They also discovered a greater variety of fracture types in naturally aged silks, perhaps indicating these fibres had been aged through a combination of processes. Miller (1986) noted similar results. Bresee and Goodyear (1986) proposed that loss of interfibrillar cohesion, rather than embrittlement, best describes what happens to naturally aged silk.

Several differences between thermally and photochemically aged silks were noted by Hersh et al (1989). Thermally aged samples were found to have discoloured 10 times more than light aged samples degraded to the same strength. For both light and heat aged samples, a decrease in strength was accompanied by an increase in amino groups, indicating scission of the main polypeptide chain. However, at any given strength, heat aged samples generated more amino groups than light aged, perhaps indicating that the mechanisms for thermal and photodegradation are different. The amounts of ammonia produced by both types of aging was almost identical.

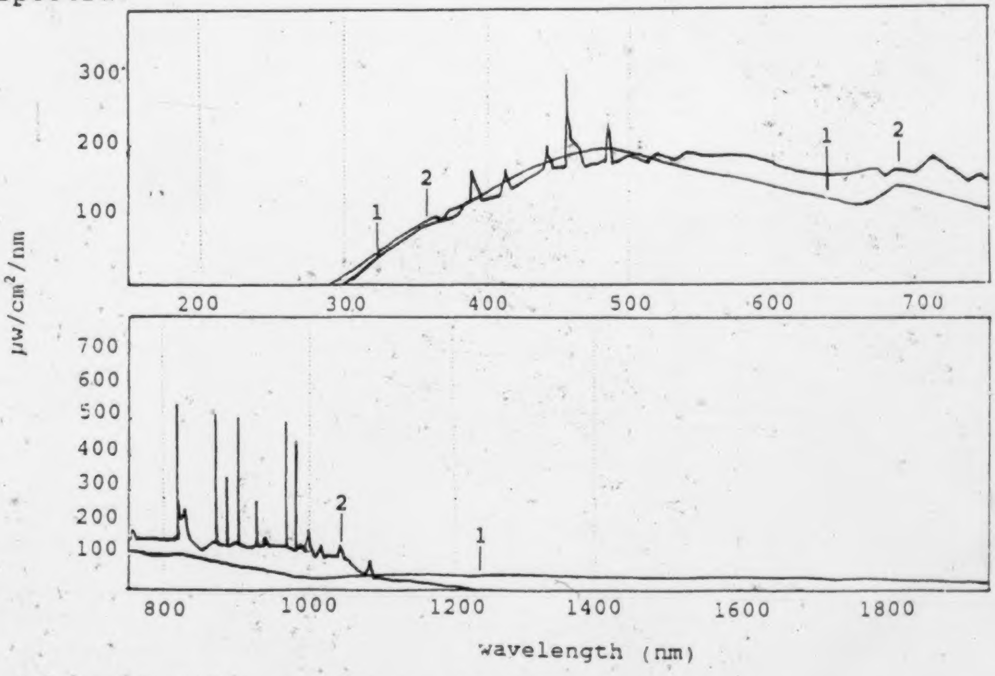
Accelerated Aging of Silk

There is no way to accurately simulate naturally aged silk. Nevertheless, artificially aged silk is often used in conservation research because it is easily produced in the lab, thus allowing for a large sample size. Also, variables can be more easily controlled when using artificially aged silk because the way in which it was degraded is known. Historic silk has been exposed to unknown forces and may contain unidentified impurities, both of which will affect results. For these reasons, the use of artificially aged silk yields more reliable results.

Silk can be photochemically aged using either natural sunlight or a simulated solar spectrum. One problem with the use of natural light to artificially age samples is the seasonal fluctuation of UV light reaching the earth's surface which causes difficulty in comparing studies done at different times of the year. Because there are many factors involved in weathering, and because of the length of time needed to chart their effect, lab equipment simulating weathering conditions has been developed. Through controlling relative humidity, temperature and light intensity, the rate of degradation can be accelerated.

Because variables can be carefully controlled using these laboratory instruments, the reliability is better than for the methods using natural light exposure. However, according to Wall and Frank (1971), "Although the xenon arc has been found to compare more closely to sunlight than the carbon arc, laboratory test methods cannot be relied upon to give forecasts of behaviour of textiles in use" (p. 33). Thus in using this equipment, some validity is sacrificed for the sake of reliability.

Carbon arc and xenon arc lamps are most frequently used to simulate daylight. Figure 2 compares the spectra emitted by a xenon arc lamp with borosilicate filters to the daylight spectra.



1. Noon daylight at Chicago, Ill. Sept. 22, 1966.
2. Water cooled xenon lamp 5500 watts, 7740 borosilicate inner and outer filters, lamp age 100hrs.

Figure 2. Spectral distributions of daylight and a filtered xenon arc lamp.

Note. Adapted from "New Developments in Water-Cooled Xenon Lamps for Lightfastness and Weathering Tests (Part I)" by J. D. Conner, 1969, *Canadian Textile Journal*, May 15, p. 50. Adapted by permission.

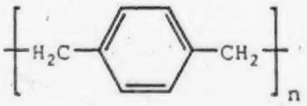
A study by Norton, Kiuntke, and Connor (1969) attempted to make the xenon arc spectrum more similar to that of noon sunlight plus skylight through the use of various filters and wattage. Xenon arc equipment is frequently used for accelerated aqing studies on silk, most often using AATCC test method 16E-1982 as a guide (Becker, 1988; Hansen & Ginell, 1989; Hersh et al., 1989; Kuruppillai et al., 1986; Miller, 1986; Poffenroth, 1990).

Parylene

The parylene group of polymers is presently being studied as a new way of dealing with delicate museum artifacts. The nature of this coating will be discussed under three main subject headings. First, the unique deposition process for parylene and the mechanism by which it polymerizes will be explained. Second, the physical and chemical properties of parylene films will be examined. Exploration of these properties reveals many of the polymer's attributes which make it suitable for use in conservation. This information is important also, because according to Fix (1981), "Since polymer degradation is a function of the energy and chemistry of the environment and polymer, a fundamental understanding of its chemistry, physics and mechanics is required to properly evaluate and predict degradation" (p. 483). The last section of this review will discuss the wide uses of these polymers, focusing on studies for use in artifact conservation.

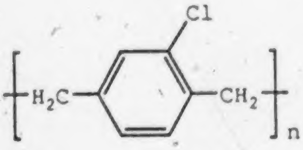
Parylene Structure and Nomenclature

Parylene is the generic name for the poly-paraxylylene series of polymers (Baker, Fix, and Judge, 1980). The term is also used, when capitalized, as the trade name for these polymers (Reed, Schramm, & Clark, 1973). Poly-paraxylylene's molecular structure consists of alternating benzene rings and methylene groups in a straight linear chain:



[18]

The unsubstituted variety is frequently referred to as parylene N. The other most frequently studied type is polychloro-*p*-xylylene, or parylene C, for which one hydrogen on the benzene ring has been replaced by a chlorine atom (Nova Tran, 1990):



[19]

Less common varieties include parylene D with two chlorine substitutions (Reed et al., 1973). and parylene M which has a methyl group added to the ring (Spivack, 1972). Many other substituted varieties have also been studied (Gorham, 1966).

Polymerization and Deposition of Parylene

History

Poly-paraxylylene was first polymerized by Szwarc by flash pyrolysis of p-xylene. Even at the high temperature of 1150 °C, this method only produced a 25% yield of the polymer and other side products were formed (Iwatsuki, 1984). The polymer has also been formed with varying degrees of success through chemical syntheses which are summarized in Iwatsuki's review article (1984). Gorham (1966) reported the polymer constituted by these techniques was usually in the form of a white powder, not a film.

In 1966, Gorham introduced a new vapour-coating technique for polymerization, which offered several advantages over previous methods. The lower pyrolysis temperature allowed the technique to be used on halogenated poly-paraxylylenes. It produced a higher yield free of by-products. Also, the polymer produced was linear and free of cross-linkages (Gorham, 1966; Iwatsuki, 1984).

Gas Phase Polymerization

Explanations of Gorham's vacuum deposition process are found in numerous sources (Gorham, 1966; Humphrey, 1984; Iwatsuki, 1984; Szwarc, 1976) and are best illustrated by Figure 3.

First, the cyclic dimer di-paraxylylene is placed into the vaporizer and heated to approximately 150° C, causing this white powder to sublime into a gas. The gas then travels to

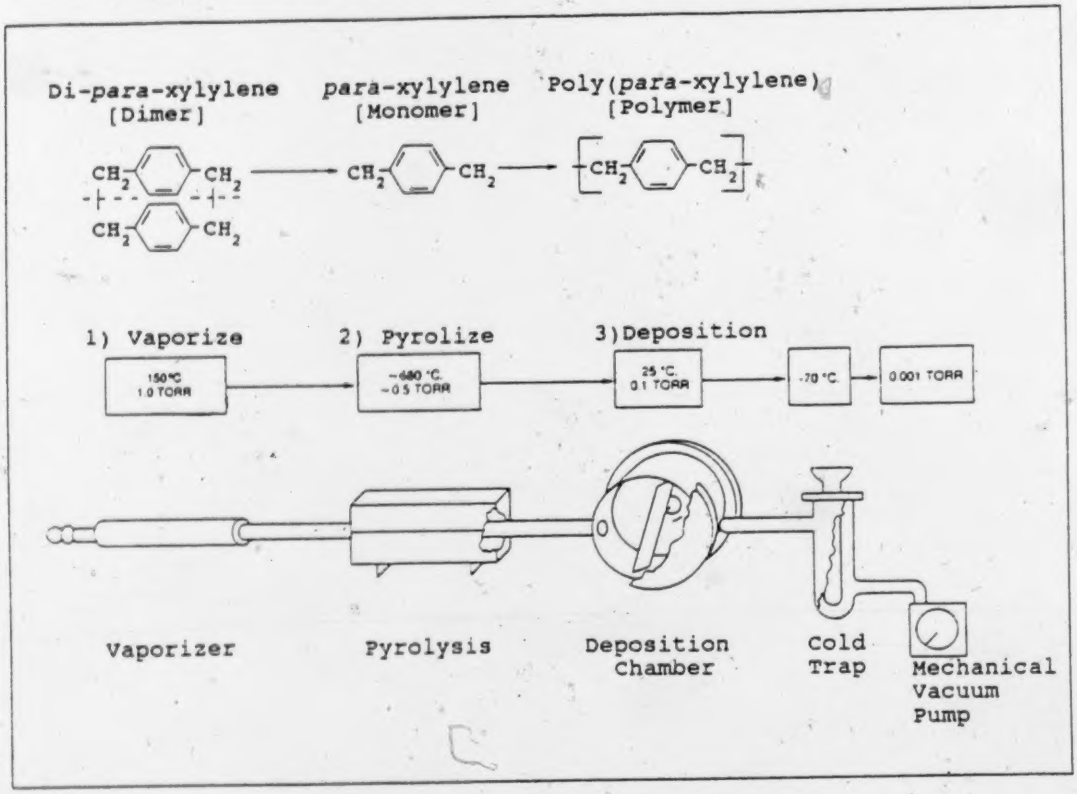
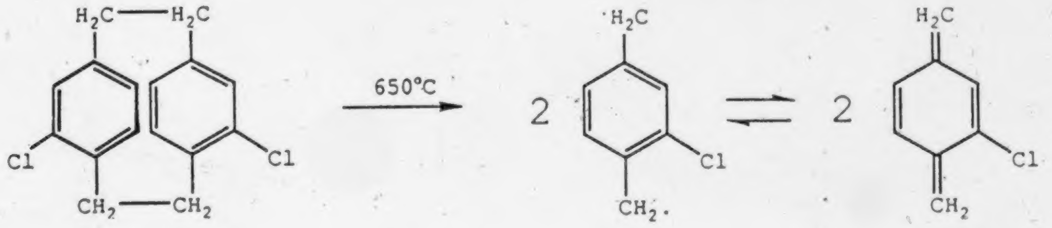

Di-*para*-xylylene
[Dimer]
para-xylylene
[Monomer]
Poly(*para*-xylylene)
[Polymer]
CH2
CH2
CH2
CH2
CH2
CH2
CH2
CH2
1) Vaporize
2) Pyrolize
3)Deposition
150°C
1.0 TORR
~680 °C.
~0.5 TORR
25 °C.
0.1 TORR
-70 °C.
0.001 TORR
Vaporizer
Pyrolysis
Deposition
Chamber
Cold
Trap
Mechanical
Vacuum
Pump

Figure 3. The parylene deposition process.

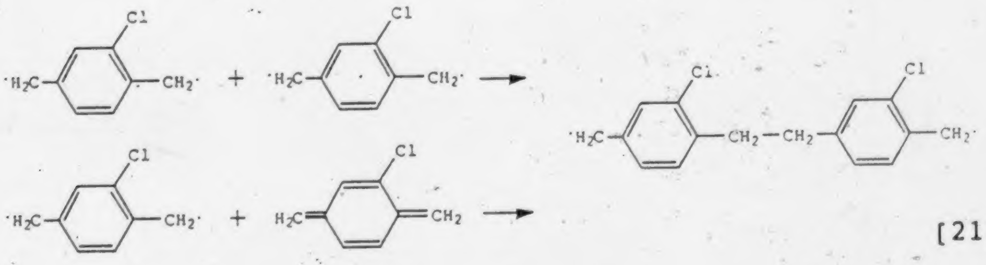
Note. From *Parylene Conformal Coatings Specification and Properties* (p.3) by Nova Tran Corporation, 1990, Clear Lake WI: Author. Copyright 1990 by Nova Tran. Reprinted by permission.

the furnace, where at 650 °C to 690 °C pyrolysis occurs, splitting the dimer into two very active monomers:



[20]

The monomers may be in either the quinoid or diradical form (Gazicki, Surendran, & Yasuda, 1985). The monomers then flow into a chamber where the item to be coated has been placed. The chamber is at room temperature and is under vacuum of approximately 0.1 torr. The high energy monomers bounce around the chamber until they have lost sufficient energy to adsorb onto the cool surfaces within the chamber. Then the monomers initiate polymerization by combining to form a diradical dimer (Gazicki et al., 1985):



[21]

The incoming monomers react with the radical at either end of the chain to increase its length by one unit. The polymer chains continue to propagate the reaction from both ends with no cross-linking. The ends of existing chains do not often react with each other because their movement is limited due to entanglement with neighbouring chains. Most monomers react with the polymer chains rather than with other monomers (Beach, Bassett, & Austin, 1989).

The polymer reacts only with itself, not with the substrate, causing the coating to be mechanically, but not chemically bonded to the surface (Loeb, Bak, Salcman, & Schmidt, 1977). If the surface is porous the monomers have sufficient energy to penetrate deeply. Starting from these centres the polymer continues to grow outward, thus providing a strong mechanical bond to the substrate (Humphrey, 1990).

Polymerization proceeds in this manner both on and beneath the surface of the growing film (Humphrey, 1990). Theoretically, the process continues indefinitely because termination due to reaction with active mono-radicals, or through the formation of ring-structures is not favorable (Szwarc, 1976). However, as polymerization continues, the growing chains become buried in the thickening film. Because incoming monomers react with centres close to the film surface, older growth centres eventually become buried and 'starved', ceasing to grow (Szwarc, 1976). Clearly, polymerization also ceases when the supply of incoming monomers is stopped (Humphrey, 1990). After deposition is complete, the free radical ends are converted by reactions to oxygen (Beach et al., 1989). No liquid phase between the gaseous monomer and the solid polymer has yet been isolated (Humphrey, 1984, 1988).

The thickness of the coating is determined by the amount of the original dimer used. When calculating the amount needed, the microscopic surface area of porous materials, like paper and textiles, must be taken into account (Humphrey, 1984). The material, shape, and morphology of the substrate have also been observed to affect coating thickness (Sharma, Hahn & Nichols, 1988). These researchers concluded that more dimer alone does not yield thicker coatings of high quality. Increased dimer elevates the system pressure and higher pressure was shown to produce electronically weak, opaque, nonuniform films. A more uniform coating can be achieved by lowering the pressure in the system either by reducing the sublimation temperature or modifying the sublimation tube geometry. Emphasis has also been placed on the need to balance vacuum pressure with pyrolysis temperature to produce high quality coatings (Williams & Rowen, 1987).

Sometimes an exact measurement of the coating thickness is essential. Kim, Powers and Mason (1982) developed the use of optical reflectometry to monitor thickness during the coating process.

Numerous studies have been conducted on various aspects of the vapour-deposition process. In their investigation of paraxylylene coatings, Baker, Bagdasarian, Fix and Judge (1977) altered vaporization/pyrolysis temperatures and deposition load, and studied the films produced. Chamber pressure and deposition rate were also studied. Among their conclusions they stated that "electrical, mechanical and physical properties of the film are essentially unchanged with minor variations in the deposition conditions"(Baker et al., 1977, p. 900). The same conclusion was also drawn by Loeb (1971).

The penetration of monomers into narrow channels was the subject of a study by Broer and Luijks (1981). By decreasing the monomer pressure, and thereby decreasing the deposition rate, penetration was increased. In addition, polychloro-*p*-xylylene was seen to have less favourable penetration than the unsubstituted variety. This difference was likely due to the high reactivity of the parylene C monomers.

The vacuum deposition coating method has a number of favourable attributes. The parylene coating can "replicate surface irregularities down to 2400 lines/mm" (Loeb, 1971, p. 48), allowing irregular surfaces, and concealed areas to be evenly coated. Parylene is truly conformal and of uniform thickness because it thickens from all areas of the substrate outward simultaneously. The coating produced is colourless, transparent, and pinhole free down to a thickness of 0.001" (Szwarc, 1976). In addition, the process also bypasses the need for the drying and curing steps necessary in conventional technologies and does not require the use of environmentally harmful solvents (Szwarc, 1976). Because the coating takes place in a vacuum, "even highly reactive substances which are destroyed or spoiled by exposure to air or moisture can be safely coated" (Szwarc, 1976, p. 478).

The Structure of Parylene Coatings

Extensive research has been done on the molecular structure of parylene films. Beach et al. (1989) stated

> In a manner typical of crystalline polymers, the crystallinity of parylenes is normally limited to small submicrometer domains that are randomly and uniformly dispersed through a continuous amorphous phase. Adjacent polymer chains, in order to acquire greater overall system stability, would prefer to be close to one another, but the extent to which they can is limited by the tangles already present (p. 1013).

Each chain is long enough to pass through several crystallites thus providing a strengthening matrix for the bulk polymer (Beach et al., 1989).

Wunderlich (1968) indicated that at temperatures below 30 °C, crystallization occurs after polymerization begins, but before the chain growth is complete. Polymerization and crystallization occur in successive stages during the overall deposition process. Two different structures for the crystalline regions of parylene N have been observed, and are temperature dependent. At ambient temperatures, crystals are of a monoclinic α form only, which is modified to a ß form above 220 °C (Iwamoto & Wunderlich, 1973; Kubo & Wunderlich, 1972). The dimensions of the α form are: a= 5.92 Å, b= 10.64 Å, c(chain axis)= 6.55 Å, ß= 134.7°, with two monomer repeat units per cell (Iwamoto & Wunderlich, 1973). The ß form has the following configuration: a= b= 20.52 Å, c (chain axis) = 6.58 ± 0.02 Å, and τ= 120°, for 16 monomer units per cell (Niegisch, 1966). The parylene C polymer has only one crystal structure, which is very similar to the α form of parylene N.

The crystal dimensions have been defined as follows: a= 5.96Å b= 12.69 Å, c (chain axis)= 6.66 Å, $\alpha=\gamma=90°$ $\beta= 135.2°$. The b axis for parylene C is slightly longer than for parylene N due to the chlorine atoms protruding from the benzene rings (Isoda, Ichida, Kawaguchi, & Katayama, 1983).

Within the α crystals, the benzene rings are parallel to each other and are oriented in the same direction. The rings are parallel to the b axis of the crystal. Greatest stability occurs when this b axis is oriented perpendicular to the substrate surface (Iwamoto & Wunderlich, 1973). Within the crystalline regions, the polymer chains with their constituent benzene rings have a preferred orientation; however, in the rest of the bulk polymer, the chains are completely random showing no preferred orientation (Beach et al, 1989).

Properties of Parylene

The physical properties of parylene are affected by the presence of different substituents on the benzene rings. Table 3 summarizes the properties of the unsubstituted and chlorinated types, parylene N and parylene C.

Mechanical Properties

Parylene C has the highest tensile strength and tensile modulus of the parylene family (Gorham, 1966). Parylene C also has an impressive elongation at break of 220%. The elongation at break for parylene N is highly variable, ranging from 10% to 15% (Gorham, 1966) to up to 250% (Nova Tran, 1990).

Spivack (1972) tested both the uniaxial and biaxial mechanical properties of very thin films (0.12 μm to 0.28 μm). He calculated the rupture constant as an indication of biaxial or burst strength, taking pressure to rupture, film thickness and diameter of the unsupported film into account. In keeping with Gorham (1966), he found parylene C to have superior mechanical properties to parylene N and concluded that the thickness of film appeared to have very little effect on

Table 3
Properties of Parylene

Properties[a]	Parylene C	Parylene N[b]	Method
	Mechanical and physical properties		
Density (gm/cc)	1.289	1.10-1.12	ASTM D1505-57T
Index of refraction (N_u^{23})	1.639	1.661	Abbe refractometer
Tensile strength (psi)	10 000	6000-11 000	ASTM D882-56T 10% strain/min
Young's modulus (psi)	400 000	350 000	ASTM D882-56T 1% strain
Elongation to break (%)	200	20-250	ASTM D882-56T 10% strain/min
Water % absorption (24hr)	<0.1	<0.1	ASTM D570-57T
	Thermal properties		
Melting point (°C)	280	405	Secant modulus-temp. curve (1)
Glass transition temperature (°C)	80-100	60-70	Secant modulus-temp. curve (1)
	Electrical properties		
Dielectric strength (volts/mil, short time, 1 mil film)	5600	7000	ASTM D149-64
Dielectric constant 60 Hz	3.15	2.65	ASTM D150 65T 1-in^2 mercury electrodes

Continued

Table 3 (continued)
Properties of Parylene

Properties[a]	Parylene C	Parylene N[b]	Method
Barrier properties			
Gas permeability cc-mil/100 in^2-24hr			ASTM D1434-63T
N_2	0.6	15	
O_2	5	55	
CO_2	14	420	
H_2	110	540	
Moisture vapour transmission gm-mil/100 in^2 -24hr	0.21	1.6	ASTM E96-63T

Note. From *Parylene Conformal Coatings Specifications and Properties* (pp. 4-7) by Nova Tran Corporation, 1990, Clear Lake WI: Author. Copyright 1990 by Nova Tran. Adapted by permission.

[a] Properties measured on films 0.001 to 0.003 inches thick, except where specified

[b] Properties depend somewhat on deposition conditions

uniaxial tensile properties. The exception was ultimate elongation of parylene C, which varied from 65% to 345% with increasing film thickness. From his results, Spivack rated parylene C as tougher than parylene N, implying more work was required to rupture the film. Data published by Loeb (1971) show similar trends to Gorham (1966) and Spivack (1972).

Beach et al. (1989) note mechanical properties can change considerably with age. When the crystallinity of the coating increases with age, the extension decreases while the modulus and tensile strength increase.

Electrical Properties

Parylenes, in general, are good insulators (Loeb, 1971). Parylene N, because of its nonpolar and highly symmetrical nature, is an extremely good insulator making it useful in the electronics industry. Electronically continuous films can be prepared as thin as 0.5 μm (Gorham, 1966).

Barrier Properties

Research has shown parylene to be highly impermeable to water vapour. Both Loeb (1971) and Gorham (1966) found parylene C to be substantially less permeable than parylene N to water vapour and all other gases tested on 1 mil thick films (see Table 3). Parylene C has better moisture barrier properties than almost all other plastics (Nova Tran, 1990)

Water vapour transmission was also studied by Kale (1978). Standard porosity fixtures were coated and sealed with a 0.36 mil coating of parylene C. After 72 hours in a desiccator with 100% relative humidity at 25 °C, the fixtures were weighed, and the mass compared with the initial mass. The mass of moisture which had been transmitted (28.6 mg), is equivalent to a water vapour transmissibility of 23.2×10^{-10} cc(STP) $cm/cm^2 \cdot sec \cdot cm$ Hg.

Optical Properties

The parylenes absorb only the shorter wave lengths in the high energy ultraviolet portion of the spectrum, absorbing strongly in the region below 280 μm (Nova Tran, 1990). They are transparent and colourless to visible light (Beach et al., 1989). Unstretched parylene N films have a negative birefringence of -0.075 ± 0.001 (Corley, Haas, Kane & Livingston, 1954).

Solubility

Parylene N and parylene C are insoluble under most conditions. Solvents are capable of entering the amorphous phase of the polymer which causes some swelling; however, the solvent cannot penetrate the crystalline areas, provided the temperature is below the melting point of the crystallites.

The crystalline regions are therefore responsible for the high solvent resistance of the coating (Beach et al, 1989). Parylene N will only dissolve in high boiling solvents like benzyl benzoate, above 200 °C. Parylene C is slightly more soluble in these solvents (Gorham, 1966).

Degradation of Parylene

Hydrolytic Degradation

Hydrolytic degradation of parylene is chemically impossible because the coating does not react in any way with water (Beach et al., 1989).

Oxidative Degradation

There is one significant undesirable factor related to the basic properties of these polymers: "Poly-*p*-xylylene is sensitive to degradative attack by oxygen, which can detrimentally affect their useful lifetimes at temperatures in excess of 100° C in air" (Szwarc, 1976, p. 479). A study by Modica, Di Renzo, Tempesti, and Mazzocchia (1988) concluded that chlorinated parylene had a slower degradation rate than the unsubstituted type (1988).

The chapter on oxidative degradation (pp. 79-148) in *Aspects of Degradation and Stabilization of Polymers*, by Kamiya and Niki (1978) gives an excellent introduction to this complex process. The free radical reaction involved in oxidation must be initiated by thermal, photochemical, mechanical or other energy sources.

> Various oxygen-containing groups are introduced along the polymer chain or at its ends by oxidation, and some low molecular weight products are also formed. The oxidation of polymers also causes deterioration in physical properties. As the oxidation proceeds, decrease in molecular weight and discoloration of the polymers are observed. (p. 81)

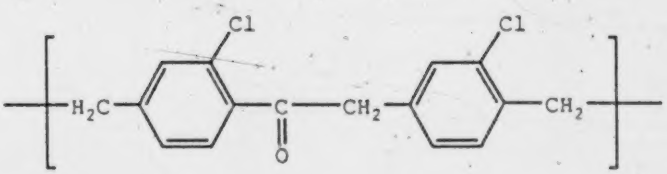
Oxidative chain scission is the primary mode of degradation for the parylenes (Beach et al., 1989).

Exposure to Heat

Parylene is able to retain its strength at high temperatures because the fortifying structure provided by interconnected crystalline regions remains strong even above the polymer's glass transition temperature (Beach et al., 1989). However, these researchers also reported elongation at break decreased dramatically from 45% to 0% after 100 hours at 150 °C in air. They state that annealing through heat exposure produced an increase in the polymer's crystallinity, which resulted in a lower elongation.

Oxidative degradation of parylene is a problem at temperatures over 100 °C when air is present. A study on the thermal degradation of parylene was conducted by Nowlin, Smith and Cieloszyk (1980). Using neutron activation oxygen analysis, they found the oxygen content of parylene C films increased with thermal aging time, but that the rate of uptake decreased with time. The decrease in rate may be due to a decrease in the amount of polymer accessible to oxidation. The release of volatile, oxygen-containing degradation products during aging may also be a factor (Nowlin et al., 1980). Change in mechanical properties was only evident after 3500 ppm of oxygen, or 1 oxygen atom per 38 monomer repeat units, had been incorporated into the film. Degradation of mechanical properties occurs when main chain scission or cross-linking occurs. Because a large amount of oxygen was present in the film before loss of strength occurred, the researchers concluded the reactions leading to chain cleavage were less frequent than those leading to the introduction of carbonyl groups (Nowlin et al., 1980)

IR characterization of the oxidated films showed the intensity of the carbonyl absorbance band (1695 cm^{-1}) increased with aging time, indicating an increase in this functional group. Interpretation of the IR readings also suggested one oxidation product to have the following structure (Nowlin et al, 1980):



[22]

An IR absorption peak at 1700 cm^{-1} in oxidated films was attributed to the presence of organic acid functional groups (COOH) by other researchers (Baker, Fix & Judge, 1980: Fix, 1981). This peak increased in intensity as a function of time and temperature.

The problem due to oxidation was addressed by Baker et al. (1980) who tested parylene C films to which an antioxidant had been added. The 18 μm films, both treated and untreated, were subjected to temperatures of 140 °C to 200 °C for up to 500 hours in a forced air oven, and the amount of oxidative degradation was measured. Fourier transform infrared spectroscopy was used to detect the presence of by-products from the oxidative process. A 180° bend test was also conducted to measure the amount of embrittlement. The study found the addition of the antioxidant increased the service life of the film by greater than five times. Lower temperature lifetimes were extrapolated from the results. According to this study the untreated film would last 11 years at 80 °C, the modified one, 58 years.

In research which expanded on the studies by Nowlin et al. (1980) and Baker et al. (1980), Grattan and Bilz (1991) investigated thermal stability as it related to artifact conservation. They exposed 10 μm to 20 μm films of parylene C and parylene N to temperatures ranging from 150 °C to 201 °C. Some of the films contained an antioxidant. Results demonstrated that as the films oxidized, yellowing and embrittlement occurred. Yellowing was not visually perceptible until the films were too fragile for instrumental colour readings to be taken. Interpretation of IR spectra revealed the rate of carbonyl formation was faster at higher temperatures. Parylene C was also seen to be more stable than parylene N and the rate of carbonyl formation decreased with time, thus confirming findings by Nowlin et al. (1980).

Grattan and Bilz (1991) also extrapolated their results to predict the films' lifetimes at 25 °C. Even though such extrapolation was acknowledged to be imprecise, results showed both parylene C and N to be extremely stable materials; for example, parylene C was predicted to have a lifetime of approximately 132,000 years in darkness at 25 °C. With this inherent stability, the Grattan and Bilz study questioned the need for adding an antioxidant for conservation purposes. Grattan (1990) has also reported when parylene with a phenolic antioxidant was used to coat books, a bright yellow discolouration appeared in highly degraded areas. The colour change was thought to be caused by a reaction between the antioxidant and the paper degradation products.

Exposure to Light

The heat-induced oxidative degradation of parylene is accelerated by exposure to ultraviolet light (Beach et al., 1989). In an internal report obtained from the Nova Tran Corporation, free parylene C films were exposed to a high intensity UV light source in air for intervals up to 300 hours after which the films were yellowed and embrittled. An infrared spectrum of the samples exposed for 72 hours showed a peak at 5.9 μm indicating the formation of carbonyl groups which are an indication of oxidative activity.

As part of the study on parylene-coated silk, Hansen and Ginell (1989) exposed 12.5 μm films to a xenon-arc lamp filtered to simulate sunlight for 500 hours. An IR filter, and a water-cooled support plate were used to reduce the heating of the samples. UV filters with cut-off points at 305 nm, 345 nm, 385 nm and 400 nm were tested to determine the wavelength threshold for yellowing. UV light sensitivity was measured through colour difference. The research revealed significant yellowing did not occur at wavelengths greater than 385 nm. Other properties, such as change in flexibility or strength, were not tested.

Exposure to Chemicals

Parylene C and parylene N are highly unreactive compounds. According to Reed et al. (1973), their chemical resistance is "very good".

Uses of Parylene

The unique properties and method of deposition of parylene have made it useful in many areas. The polymer can be used both as a coating and as an unsupported film. Parylene C is used more frequently than parylene N (Humphrey, 1986). This may be due to its superior performance in the various tests cited previously.

General Uses

As a conformal coating, parylene's primary application has been in the electronics industry where it is used to protect delicate microcircuitry from chemical and particulate contamination; its mechanical, electrical, and conformal properties make it will suited to this purpose (Kinser, 1980; Szwarc, 1976).

The coating also has potential in medicine as it is compatible with the human biosystem (Szwarc, 1976). Because the polymer is resistant to hydrolytic attack, it does not degrade while inside the body (Beach et al., 1989). The polymer has been used successfully for insulating microelectrodes in neurophysiological research. The coated electrodes are capable of monitoring nervous tissue over extended time periods (Loeb et al., 1977). It has also been used as a protective coating for pacemakers (Olson, 1980).

The coating is also being tried as a replacement for highly polluting chromium plating as a means of protecting low quality steel from corrosion. Its barrier properties have also made it subject for study by the American military as protection against chemical warfare agents (CCI Minutes, 1989).

Unsupported films have found uses for such optical devices as beam splitters and windows for soft x-ray spectrometers. Parylene films are unique because they can be cast more thinly than other substances, and have no inherent stresses due to stretching (Szwarc, 1976).

Uses in Artifact Conservation

In recent years, studies have been carried out investigating the possibility of using the parylene coating technology to consolidate fragile museum artifacts. Thicknesses in the range of 2 to 25 μm are generally used depending on the substrate (Humphrey, 1988). Studies have been conducted at institutions including the Royal British Columbia Museum, Library of Congress, The American Museum of Natural History, John Hopkins University, The Getty Conservation Institute, and the Canadian Conservation Institute (Humphrey, 1988, 1990).

Miscellaneous artifacts.

The Canadian Conservation Institute has conducted tests on a wide variety of substrates, a brief summary of which appeared in the *CCI Newsletter* (Grattan, 1989). This article focused on the success of the coating in consolidating very fragile cones and leaf mats from the Arctic Fossil Forest. A conference paper presented by Grattan (1990) discussed these applications in more detail.

In addition to its highly successful use on the cones and leaf mats, the coating has also been beneficial in strengthening crustacea and marine specimens which become dry and brittle with age. Results were generally satisfactory when parylene was used to prepare natural history artifacts for exhibit; fragile specimens could be handled more safely. Fossilized material is susceptible to cracking with changes in relative humidity. Parylene showed limited success in inhibiting the humidity-induced dimensional changes which causes this damage (Grattan, 1990).

Many ethnographic artifacts cannot be consolidated with parylene because they cannot withstand the moisture loss which occurs when the coating chamber is evacuated. The moisture loss in fur pieces resulted in contraction and irreversible distortion of the artifact. Powdery pigments were successfully stabilized with 4 μm or 8 μm coatings, but the leather, parchment, bark and cedar substrates became warped (Grattan, 1990).

Paper and books.

The coating causes a minimal change in the appearance of paper. A very slight colour change may be perceptible on some papers, and those with a shiny surface may become slightly more shiny (Humphrey, 1990). Sometimes rainbow-like interference bands occur on smooth papers like coloured plates. These are apparent on areas of the substrate which have a slightly thinner coating, due to "extreme challenges to gas penetration" (Humphrey, 1990, p.58). Parylene causes a change in texture of the paper, imparting a slippery feeling.

A series of tests were conducted by Humphrey (1984, 1986, 1990) on the effect of the coating on books and papers. Treated and untreated paper from a 20 year-old paperback book were subjected to a number of tests, including a flex stress test and water immersion tests. Untreated paper failed the flex test after 85 complete flexures, whereas the coated page showed little sign of breakage after 1000 flexures. Microscopic examination revealed most of the paper fibres were broken in the flex region, but that the paper was being held together by a web of polymer bridges.

After six months of immersion in water, the coated paper showed no sign of damage, whereas untreated samples were limp and easily damaged. The coating was also tested for weathering resistance. Again, the coated papers showed very little sign of deterioration. Some shrinkage was noted, but there was no mention of any yellowing as was observed in the light-aging study by Hansen and Ginell (1989).

Tests conducted at CCI found coated newsprint to have a

42% increase in tear strength (Grattan, 1990). Parylene acts to strengthen paper in two ways. It provides a tough coating for each individual fibre thus increasing the overall strength of each fibre. Interfibre bonding also serves to increase the overall paper strength; the film produces a bond wherever the fibres cross. The strengthening effect of the polymer is determined in part by the type of paper, and its state of degradation. Weak papers exhibit a greater percent increase in strength than do strong papers with the same coating thickness (Humphrey, 1990).

Gas-polymerization is well suited for the coating of entire books. The book is held upright in a special frame and when evacuation occurs, the pages fan-out allowing the gas to coat each individual page (Humphrey, 1986, 1988, 1990). Due to the penetration properties studied by Broer and Luijks (1981), the parylene monomers have sufficient energy to travel down the tiny spaces between the pages of a fanned book. Parylene N is preferred over parylene C in the coating of books because of its superior penetration properties. Humphrey (1990) noted that the outermost edges of the pages receive a thicker coating than areas closer to the spine.

CCI found a 2 μm coating of parylene C was effective in stabilizing red-rotted leather bindings (Grattan 1990). The coating has also been used to strengthen the fragile, charred pages of an airplane log-book so that forensic scientists could use it in their investigation of a major plane crash (Brown, 1990). The treatment has been considered for some of the volumes damaged in the 1988 fire at the Academy of Sciences Library in Leningrad.

Because book embrittlement is such a large-scale problem in libraries and archives, research is being conducted to develop coating systems capable of coating 100 or more books per cycle. Current technology can accommodate only eight books per cycle (Humphrey, 1990).

Textiles.

Parylene coating technology has been used for the treatment of archaeological textiles, including those from the Windover Bog Site (Humphrey, 1990) and the Red Bay burial textiles. The Red Bay textiles were treated with a 4.4 μm coating of parylene C which was successful in preventing further shedding of wool fibres. It was suggested that the accompanying surface bloom and slight change in hand could be prevented by the application of the polymer in repeated thin layers (CCI Minutes, 1989; Grattan, 1990).

Peatified textile remains were among the items recovered from the Windover Bog Site in Florida from 1986 to 1987. These finds represent the oldest known textile specimens in the New World, having been dated to the 6th millennium BC. After an initial consolidation treatment and freeze drying, the artifacts were still in a friable and extremely delicate state. As a preliminary test, one fragment was coated with 10.6 μm of parylene N; the coating produced no observable change in appearance, yet greatly enhanced the strength of the artifact. This consolidation allowed the fragment to be handled more securely, even allowing it to be turned over to examine the other side (Humphrey, Gardner, Andrews, Adovasio, & Strong, 1990)

Preliminary investigations have been conducted on the use of parylene to stabilize New Zealand Maori textiles (Barton & Weik, 1988). The decorative black-coloured portions of these textiles have deteriorated severely due to the low pH and high iron content of the mud used in the traditional colouring process. These areas are now in an extremely fragile and powdery state, and in many cases have been lost entirely. A coating of 5.4 μm and 8.6 μm of parylene produced a substantial increase in strength. Although some change in appearance was noted, the results were still described as impressive.

Among the many materials coated at the Canadian

Conservation Institute were some degraded silk samples which were treated with 1 to 5 μm of parylene C. Interference bands were apparent on shiny fabrics which had been given coatings from 1 to 3 μm, but were not evident with the 5 μm coating. Weave structure was also seen to play an important role in flexibility change. Those fabrics with open weaves remained more flexible with thicker coatings, whereas those with more compact weave structures became stiff with even a thin coating (Grattan, 1990). Overall, those textiles with a coating of 1 μm were most acceptable and further testing of coatings from 0.1 to 1.0 μm was suggested, as was the use of SEM to examine the textiles (CCI Minutes, 1989).

The most extensive study to date on the use of parylene in textile conservation was conducted at the Getty Conservation Institute by Hansen and Ginell (1989). Tests were conducted on modern and naturally aged silk, with some variation in coating thickness. 12 μm thick films were also used in the previously cited UV light study.

Increased coating thickness (uncoated to 1.5 μm) on modern silk was seen to increase its tensile strength initially. Coated modern silk samples were then aged in a convection oven. Results from this test indicated that parylene C had no effect on the heat thermal degradation rate of silk's tensile properties; however, the researchers noted the coating may suppress degradation at room temperature because at this lower temperature the coating is a superior barrier to gases and water vapour. In addition, the researchers found untreated silk deteriorated faster above 50% relative humidity, and the addition of parylene C did not alter that rate (Hansen & Ginell, 1989).

The pliability of brittle historic silk was not found to increase with the addition of the coating (Hansen & Ginell, 1989). These results contrast with those of Humphrey (1984) who found the polymer aided paper in resisting breakage through flexing. The initial modulus and breaking load of historic silk were improved with the coating (Hansen & Ginell, 1989).

Coated modern and coated historic fabrics were also exposed to a xenon arc Weather-Ometer simulating unfiltered sunlight. Both coated and uncoated samples yellowed upon exposure to light; however, the coated fabrics continued to yellow, whereas the uncoated stopped after 50 kJ of exposure. The strength of both coated and uncoated samples continued to decline up to 242 KJ exposure. Although coated samples were initially stronger, after 242 kJ (340 nm) the strength of coated and uncoated samples was similar.

From their research, Hansen and Ginell (1989) concluded that the coating could be considered for treatment of very degraded silk where an increase in tensile strength was of prime importance such as for static display. They strongly advocated the use of filters or special lamps to eliminate wavelengths below 400 nm because the coating was most sensitive to ultraviolet portion of the spectrum.

The use of coating technology on textiles is feared to reduce the drape of coated fabrics. Drape is determined by the ability of the fabric yarns to move and slip past one another at cross-over points. Whether a parylene coating would cause these yarns to weld together, and hence inhibit drape, is thought to be determined by coating thickness and yarn dimension (CCI Minutes, 1989).

Reversibility.

Ideally, conservation treatments performed on objects should be able to be removed or reversed without a detrimental effect on the artifact. In this way, if the treatment is unsuccessful, retreatment is possible (Grattan, 1990). In actual practice very few treatments, if any, are strictly reversible. For example, cleaning causes irreversible removal of dirt and other substances from the artifact. The removal of stitching often leaves holes in textile artifacts. Nevertheless, the concept of reversibility is important in conservation ethics, and needs to be addressed concerning parylene coating treatments.

Because these polymers are highly crystalline, they have great resistance to solvents (Pascoe, 1985). Olson (1986) suggested several methods for selected removal of the coating from high performance printed wiring boards. Unfortunately, none of these techniques, which include exposure to high temperature, and use of wire brushes and abrasive powders can be applied to coated artifacts. For these reasons, such a treatment is irreversible; however, in the case of highly deteriorated objects where immediate consolidation is essential for the survival of the artifact, reversibility may not be of paramount importance (Pascoe, 1985). The coating may be the only treatment option for some artifacts, or may give superior results compared to more traditional treatment methods. Also, the coating does not prevent further consolidation and treatment from being performed (Grattan, 1990).

CHAPTER 3 MATERIALS AND METHODS

Fabrics

Both artificially and naturally aged silk fabrics were used in conducting this research. Bresee & Goodyear (1986) and Hersh et al. (1986) also used a combination of artificially and naturally aged samples in their research on silk degradation. Artificially aged silk can be produced in the laboratory and allows for a large number of specimens. Because artificial aging does not replicate natural aging, naturally aged silk fabrics were also used in order for the results to be valid regarding historic artifacts. Modern silk was not coated and tested because it was studied in depth by Hansen and Ginell (1989).

Historic silk fabrics were donated for study by the Clothing and Textiles Collection at the University of Alberta. A variety of fabrics was selected based on size, weight, weave, presence of dye and weighting agents, and degree of degradation. An undyed, unweighted degummed silk fabric with a twill weave (#609 from Testfabrics)[1] was used for the artificially aged samples. A description of each fabric appears in Table 4.

All fabrics were carefully wet-cleaned using a 0.2% solution of Shurgain® anionic detergent in distilled water to remove dirt and other impurities. A standard cleaning method for historic textiles was followed (Appendix A-1). After washing, the new silk twill fabric (fabric 8) was artificially aged using a 300 kJ exposure in a xenon-arc Weather-Ometer. A detailed description of this procedure is found in Appendix A-1.

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[1] TestFabrics Inc., P.O. Drawer O, 200 Blackford Ave., Middlesex NJ, 08846

Table 4

Descriptions of Naturally and Artificially Aged Silk Samples

#	Size (cm)[a]	Weave	Colour	Weighted	Condition
			Naturally aged fabrics		
1	11 x 668	plain	plum	yes	splitting
2	15 x 940	satin	black	yes	stable
3	51 x 559	plain	turquoise	yes	brittle splitting
4	49 x 280	plain	maroon	yes	brittle breaking
5	44 x 103	plain crepe	undyed	yes	stable
6	84 x 142	plain crepeline	undyed	no	stable
7	192 x 40	plain	undyed	no	stable
			Artificially aged fabric		
8	100 x 200	twill	undyed	no	stable

[a] Filling x Warp

Sampling Procedure

Warp specimens measuring 14 x 7 cm (LxW) were cut from the new washed fabric 8 prior to artificial aging. Specimens were cut in a staggered fashion, and visible flaws in the fabric were avoided as shown in the cutting diagram in Appendix A-2. No specimens were taken from within 50 mm of each selvedge.

The naturally aged fabrics were cut into panels measuring approximately 17 x 48 cm (LxW). Eight panels were cut from fabric 4, 6 and 7, and sixteen panels were cut from fabrics 2 and 3 to provide extra sets of samples to use if necessary.

The eight panels cut from fabric 5 were smaller (17 x 24 cm) due to the limited amount of this fabric. Fabric 1, a narrow ribbon-like fabric was cut into 49 x 11 cm strips. In all cases, obvious holes, splits and discolourations were avoided as much as possible, in order to minimize differences among samples.

The panels of naturally aged silk were then randomly assigned to coating treatment groups; four of the eight panels from each fabric were assigned to group 1 which remained uncoated, the other four to group 2 which were coated with the parylene C polymer. The artificially aged specimens were also randomly assigned to these two treatment groups.

Application of the Parylene-C Coating

The specimens in group 2 were transported to the Nova Tran Laboratory in Clear Lake, WI for coating in a Parylene Deposition System model 1050. To fit into the vacuum chamber conveniently, the 17 x 48 cm panels were cut in half to produce 17 x 24 cm (LxW) specimens. Each of these specimens was placed on a wire mesh rack and twenty-five racks were stacked into a holder for coating. Glass reference slides were placed with the specimens on the top, middle and bottom racks, and were used to measure the coating thickness on the fabric. The specimens were coated in four batches as shown in Table 5.

The holder containing the stacked specimens was placed in the vacuum chamber and the chamber pressure was reduced to 20 mTorr. For each batch, a conservative estimate was made to determine the amount of Parylene-C dimer needed to produce a coating approximately 0.8 μm thick. After deposition was complete, a profilometer was used to measure the coating thickness on the glass reference slides. It was assumed the coating thickness deposited on the slide was the same as the coating thickness on the specimens. If the coating was too thin, the polymerization process was repeated again until the

Table 5
Parylene-C Coating of Silk Fabric Specimens

Batch #	Fabric #	Rack #^{a}	Dimer^b amount	Coating^c thickness
1	6	1 to 8	9	0.88
	5	9 to 16		0.70
	7	17 to 20		0.60
2	3	1 to 16	18	1.00
	4	17 to 24		1.00
3	1	1 to 6	12	0.74
	2	7 to 22		0.74
4	8	1 to 24	7	0.85

[a] racks in specimen holder numbered from top to bottom
[b] mass (g) of dimer placed in vaporizer
[c] in micrometers

desired thickness was reached. The three reference slides in batch 1 showed a slight gradation in coating thickness from the top to bottom of the chamber which was corrected for subsequent batches. A summary of the dimer amounts used and the coating thickness produced is given in Table 5. The amount of dimer used varied because the overall surface area for each batch of specimens was different due to variation in fabric weight and the number of specimens included. The specimens were coated with a 0.8 ± 0.2 μm layer of the parylene C polymer.

Accelerated Aging

The coated and uncoated panels were cut into 14 x 7 cm (LxW) warp specimens. The artificially aged fabric specimens had already been cut to this size before coating. These specimens were then randomly assigned to the treatment groups outlined in Table 6. For fabrics 2, 3, 4, 6, 7, and 8, six

Table 6

Light Exposure Conditions Assigned to Treatment Groups

Treatment group #	Light[a] exposure conditions
	Uncoated samples
1A	control- not put in Weather-Ometer
1B	fully masked from light in Weather-Ometer
1C	exposed to light in Weather-Ometer with the ultraviolet wave lengths removed
1D	fully exposed to all wave lengths of light in Weather-Ometer
	Coated samples
2A	control- not put in the Weather-Ometer
2B	fully masked from the light in the Weather-Ometer
2C	exposed to light in Weather-Ometer with the ultraviolet wave lengths removed
2D	fully exposed to all wave lengths of light in Weather-Ometer

Note: Weather-Ometer conditions were 250 kJ/m^2 (420nm) exposure at 65 % relative humidity and a black panel temperature of 50 °C.

[a] A xenon-arc lamp filtered to simulate the solar spectrum

specimens were assigned to each treatment group. Due to the limited availability of fabrics 1 and 5, three specimens were placed in each treatment group. Groups 1A and 2A were not put in the Weather-Ometer and acted as the controls for the experiment. Specimens in groups 1B and 2B acted as a second set of controls. They were exposed to the 65% relative humidity and 50 °C black panel temperature within the Weather-Ometer but were shielded from the xenon arc rays by standard test masks. UV filtering film was placed over those specimens in groups 1C and 2C during irradiation. This transparent polyester film, supplied by University Products[2], filtered out the ultraviolet portion of the spectrum with wave lengths below 400 nm. Such a film would be readily available to the museum community through University Products' mail-order catalogue. The remaining specimens in groups 1D and 2D were exposed to all wave-lengths produced by the xenon arc lamp.

The specimens were aged in an Atlas Weather-Ometer model Ci35W using a procedure based on AATCC test method 16E-1987. The xenon arc lamp was fitted with borosilicate inner and outer filters to simulate the daylight spectrum. The specimens were inserted into standard test holders and were backed with acid-free mat board. Specimens from the same fabric underwent photochemical aging together. They were given an exposure of 250 kJ/m^2 with a lamp irradiance of 0.75 w/m^2 measured at 420 nm, which took approximately four days. The relative humidity was 65 ± 5% and black panel temperature was 50 ± 2 °C, the same conditions applied by Hansen and Ginell (1989).

Measurement of Physical Properties

Rationale

Measuring changes in physical properties is one way to monitor the degradation of silk. Hansen and Ginell (1989) tested breaking load of textile fabrics, but yarn breaking tests have also been used (Becker, 1988; Hersh et al., 1989; Kuruppillai et al., 1986; Miller, 1986; Poffenroth, 1990). For this study, fabric strength tests were chosen over yarn tests because the fabric strength test is a better indicator of the coating's overall effect on fabric structure. Also, fabric tests allowed for comparison with the results from Hansen and

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[2] University Products c/o Bury Media and Supplies Ltd.
B5-4255 Arbutus Street, Vancouver, BC Canada V6J4R1

Ginell (1989).

Colour change has been measured by Becker (1988), Hersh et al.(1989), Kuruppillai et al.(1986) and Poffenroth (1990), all of whom used the CIElab* system described below and reported ΔE* values for overall colour change. The CIELab* system was used for this research as well.

At present, no study has been located addressing the effect of the parylene C coating on the flexibility and moisture regain properties of textiles. These properties are of interest to textile conservators and therefore were measured in addition to strength and colour change.

Scanning electron microscope techniques have been used to study fibre damage due to mechanical stress, or heat and light exposure. SEM analyses of fibre fractures have been used by Bresee and Goodyear (1986) and Zeronian, Alger, Ellison and Al-Khayatt (1986) to draw conclusions about fibre degradation mechanisms. The technique may provide information on how the coating affects the fibre surfaces and fabric structure. Such observations would help clarify some of the coating's effects on flexibility and drape. The Minutes of the Parylene Review (1989) at the Canadian Conservation Institute (CCI) suggest SEM observation of coated specimens would be useful. Such analysis was not undertaken by CCI or the Getty Institute.

Colour Change

The Hunterlab D25M-9 Tristimulus colorimeter was used to measure change in colour between treated and control samples following the guidelines outlined in the AATCC Test Method 153-1985 "Color Measurement of Textiles-Instrumental". The colorimeter had a 45° circumferential incidence/0° viewing instrument geometry, which measured the specimen at the angle of least specular reflectance. The instrument utilized the 1931 2° observer, and Standard Illuminant C which is similar to the visible light portion of the daylight spectrum. Measurements were taken with a 5.1 cm specimen port.

Using the CIE 1976 L*a*b*[3] system for colour measurement, L*, a* and b* coordinates were generated to describe lightness/darkness, red/green and yellow/blue respectively. The change in colour between treated and control samples was measured in terms of change in these three colour coordinates, or ΔL*, Δa*, Δb*. A measure of overall colour change, ΔE, is related to ΔL*, Δa*, Δb* as follows:

$$\Delta E^{*}=[(\Delta L^{*})^{2}+(\Delta a^{*})^{2}+(\Delta b^{*})^{2}]^{1/2} \qquad [23]$$

where

$$L^{*}=116(Y/Y_{n})^{1/3}-16$$
$$a^{*}=500[(X/X_{n})^{1/3}-(Y/Y_{n})^{1/3}]$$
$$b^{*}=200[(Y/Y_{n})^{1/3}-(Z/Z_{n})^{1/3}]$$

and X, Y and Z are the colour response readings as taken by the instrument (Billmeyer & Saltzman, 1981). X_n, Y_n and Z_n are the tristimulus values of the white reference tile (Billmeyer & Saltzman, 1981).

The ΔL*, Δa*, Δb*, and ΔE* values of the uncoated specimens were taken by comparing the L* a* b* for each of the masked, filtered and fully exposed specimens (groups 1B, 1C, and 1D) to the average reading of the uncoated control group (1A). Two sets of delta values for the coated specimens were calculated, using both the coated control (2A), and the uncoated control (1A) as the standards for comparison with the Weather-Ometer exposed coated specimens (groups 2B, 2C, and 2D).

In addition to ΔE, a yellowness index (YI) reading was also taken on the undyed specimens (fabrics 5, 6, 7, and 8). This index was developed specifically to study yellowing due to degradation or weathering (ASTM E313-73), so is preferable to ΔE, which is a more general measure. YI is defined as follows in ASTM E313-73 "Standard Test Method for Indexes of Whiteness and Yellowness of Near-White, Opaque Materials":

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[3] The more recent CIE 1976 L*a*b* scale is recommended over the Hunter L,a,b scale

$$YI = \frac{100\,(Y - 0.847Z)}{Y} \qquad [24]$$

The colour of each 14 x 7 cm (LxW) specimen was measured on the side which faced the xenon arc lamp. Four readings were taken on each specimen, two in the warp and two in the weft direction; these readings were averaged to give the overall colour reading for the specimen. A stack of the six specimens from each treatment group was presented to the colorimeter specimen port, thus imparting opacity to the specimen being read, and preventing the white tile backing from showing through.

Flexibility

Following colour measurement, each 7 x 14 cm specimen was cut in half lengthwise to produce twelve 12 x 2.5 cm (LxW) warp test specimens. The edges which had been protected from exposure by the Weather-Ometer test frame were trimmed off. These strips were then conditioned to 65 ± 2% relative humidity and 20 ± 2 °C.

ASTM test method D1388-64 "Standard Test Method for Stiffness of Fabrics" was followed using the Cantilever Test. The strip was placed on a level platform, and a small rectangular weight placed on top of it. By moving the weight, the specimen was then slowly pushed in the longitudinal direction over the edge of the platform until the free end bent down in an arc under its own weight and touched a centimeter scale which made a 41.5° angle with the horizontal platform. The overhang distance (the distance in centimeters from the contact point on the scale to the level platform) for each strip was read four times: face up, face down, first one end and then the other. These measurements were averaged for each strip, and bending length and flexural rigidity calculated as follows:

$$\text{Bending Length} = O/2 \qquad [25]$$

where O is the length of overhang in cm,

$$\text{Flexural Rigidity (mg-cm)} = W \times (O/2)^3 \qquad [26]$$

where W is the weight per unit area in mg/cm^2 (ASTM D1388-64).

Prior to aging, the mass per unit area for each fabric was determined. Two cleanly cut 14 x 7 cm specimens were conditioned and weighed to the nearest 0.1 mg and the mass per unit area for each calculated. These two results were then averaged.

Tensile Properties

The same specimens used for the flexibility test were also used to determine the breaking load, extension at break and energy at break according to CAN/CGSB 4.2 no. 9.1-M90, "Breaking Strength of Fabrics--Strip Method--Constant time-to-break Principle". Tests were conducted using the ravel-strip method for fabrics 2, 5, 6, 7, and 8. The warp strips were produced by ravelling away yarns on each side, forming a 2.0 cm strip with a 2.5 mm fringe down each side. It was necessary to use the cut strip method for fabrics 1, 3, and 4, because some specimens were too degraded to unravel. For these fabrics, 2.5 mm were trimmed off each side to produce a test strip measuring 12 x 2.0 cm (LxW).

The testing was done under standard conditions of 65 ± 2% relative humidity and 20 ± 2 °C with an Instron Universal Testing Instrument Model 4202. Pneumatic grips with a width of 25 mm and rubber grip faces were used, and the gauge length was set to 75 mm. The cross-head speed was adjusted so the average time-to-break was 20 ± 3 seconds. Ten strips were measured for each treatment group, except for fabrics 1 and 5, where five strips were measured.

In addition to breaking strength, the Instron machine also measured energy to break and elongation. Energy to break, or work of rupture is calculated as the area under the load-elongation curve, and is a measure of overall toughness of a material. Elongation is the change in length undergone by the fabric at its breaking point. Extension at break expresses this change in length (ΔL) as a percentage of the original length (L_o) as follows:

$$\text{extension (\%)} = \frac{\Delta L}{L_o} \times 100 \qquad [27]$$

Moisture Regain

The moisture regain for the treatment groups of each fabric was determined using the procedure outlined in CAN/CGSB 4.2 no. 3-M88 "Determination of Moisture in Textiles", Procedure B. The test strips used previously for flexibility and tensile property measurements were unravelled and the yarns cut in 1 cm lengths. Those fabrics which could not be ravelled (1, 3 and 4) were cut into tiny 4 mm^2 pieces. The ravelled material for each treatment group was divided into three samples and the moisture regain measured for each of these samples. Two strips from each group were reserved for SEM analysis.

The ravelled fabric was allowed to equilibrate to standard testing conditions (65 ± 2% relative humidity and 20 ± 2 °C) for a minimum of two days. The conditioned mass was then determined on a Mettler analytical balance. Empty weighing vessels were dried to a constant mass by placing in a laboratory convection oven at 105 °C overnight. Then the vessels were removed from the oven and allowed to cool over Drierite® desiccant for one hour in glass desiccators before weighing. They were replaced in the oven for a minimum of one hour between weighings. A constant weight was achieved when successive weighings differed by less than ±0.0005 g. The specimens of known conditioned mass were then transferred to the dried containers and placed in the oven to dry at 105 °C over night. Using the procedure described above, the specimens were weighed and dried repeatedly until a constant weight had been obtained.

From these measurements, moisture regain was calculated as follows:

$$\text{Moisture regain(\%)} = \frac{\text{conditioned mass - dry mass}}{\text{dry mass}} \times 100 \qquad [28]$$

SEM Analysis

The fabrics and corresponding treatment groups selected for viewing under SEM are listed in Table 7. Because the properties of the masked samples (groups 1B and 2B) did not differ from the overall controls (groups 1A and 2A), specimens in groups 1B and 2B were excluded from SEM analysis. The fabrics chosen represent examples of dyed and weighted, undyed and weighted, naturally aged and artificially aged undyed and unweighted fabrics with a variety of weaves.

Table 7
Samples Analyzed With SEM

Fabric #	Description	Treatment groups
2	naturally aged weighted black satin	1A 1C 1D 2A 2C 2D
5	naturally aged weighted undyed crepe	1A 1C 1D 2A 2C 2D
7	naturally aged unweighted, undyed plain weave	1A 1C 1D 2A 2C 2D
8	artificially aged unweighted, undyed twill	1A 1C 1D 2A 2C 2D

A specimen 0.5 cm^2 was mounted on a stub with double-sided adhesive tape. Conductive carbon glue was applied to the edge of the specimen to increase its conductivity through the stub. The specimen was then sputter-coated with 15 nm of gold to provide a conductive surface, and viewed under various magnifications using a Cambridge Stereoscan 250 scanning electron microscope. Photographs were taken at magnifications of 1500x, 3900x and 8000x.

Energy Dispersive X-Ray Analysis (EDXA) was also performed on several specimens to determine what elements were present in the specimen. Only elements in sufficient amounts with molecular weights higher than sodium were able to be detected.

Statistical Analysis

The inter-relationship of three independent variables (type of fabric, light exposure, and presence of coating) was evaluated for each of the dependent variables. The dependent variables were: total colour difference (ΔE), yellowness index, flexural rigidity, tensile strength, extension, energy to break, and moisture regain. Guidelines given by Milliken and Johnson (1984) for analyzing studies with three-way treatment structures were followed. First, a three-way analysis of variance was performed on the data for each dependent variable to determine which main effects and interactions were statistically significant. The UANOVA procedure, available through the $Spss^x$ statistics package on the University of Alberta mainframe computer, was used. Tables summarizing which main effects and interactions were statistically significant are given in Appendix A-4. For those dependent variables in which the coating-by-light-by-fabric three-way interaction was significant, the Duncan's Multiple Range Test was performed for a two-way treatment structure (between coating and exposure) at each level of the third independent variable (fabric). In this way, the statistically significant differences among the treatment groups for each fabric were determined.

For dependant variables in which the three-way interaction was not statistically significant, the Duncan's Multiple Range Test was performed on pairs of factors that interacted in a statistically significant way. When the three-way interaction is not statistically significant, this indicates two of the independent variables, coating and exposure for example, have the same effect on the dependent variable at all levels of the third independent variable (fabric). Analysis of their effect on each individual fabric is not necessary, therefore, as the effect is the same for each fabric.

The effects of fabric structure, weighting agents, dye, and whether the fabric was naturally or artificially aged were also considered. Each fabric was assigned a binary code to indicate if it was dyed, weighted, and/or naturally or artificially aged. The raw data obtained by the physical property tests were converted to normalized data by dividing the raw data points in each treatment group by the mean of their corresponding unexposed control group. Normalized data effectively describes the change in a specific property, thus allowing the diverse fabrics to be compared to each other. The following three-way ANOVAs were performed on the normalized data set for each dependent variable: coating-by-exposure-by-age, coating-by-exposure-by-dye, and coating-by-exposure-by-weight. Summary tables of the main effects and interactions are included in Appendix A-4. Duncan's Multiple Range Tests were then performed to determine where there were statistically significant differences between groups. The effect of fabric structure was not analyzed using statistics.

CHAPTER 4 RESULTS AND DISCUSSION

In order to evaluate the long term effect of the parylene C coating on degraded silk fabric, measurements of physical properties were taken before and after accelerated photochemical aging. The exposure of the samples to accelerated light aging was conducted using two sets of controls. Control group A (unexposed) was not placed in the Weather-Ometer, and group B was placed in the Weather-Ometer but masked from the light. Group B differed from group A because it was exposed to 65% relative humidity and a black panel temperature of 50 °C for a 4 day period in the aging chamber. There was no statistically significant difference between group A and B for the properties measured, suggesting exposure to these conditions alone did not cause sufficient degradation to affect physical properties. Henceforth, all comparisons of the light exposed samples were made with control group A. Changes in colour, flexibility, tensile properties, and moisture regain were monitored. Scanning electron microscopy was also employed to detect surface changes.

Colour Change

ΔE is a measure of overall colour change, which mathematically combines the L^*, a^* and b^* numerical colour coordinates. Without reference to these coordinate values, ΔE has limited meaning, therefore the L^*, a^* and b^* values for each treatment group are given in Appendix A-3. The ΔE values for the uncoated treatment groups were calculated using the unexposed uncoated fabric as the standard. The coated fabrics in each treatment group were compared to the unexposed coated fabric. The changes in colour apparent immediately after application of the parylene C coating are summarized in Table 8. Six of the eight fabrics exhibited a statistically significant change in colour. Light coloured, or undyed

Table 8
Initial Effect of Parylene C Coating on the Colour of Silk Fabrics

Fabric description				Change in colour after coating	
#	n	Finish[a]		ΔE	SD
1	3	W	D	1.1*	0.26
2	6	W	D	3.0*	0.52
3	6	W	D	2.7*	0.96
4	6	W	D	5.1*	0.95
5	3	W	UD	0.7	0.17
6	6	UW	UD	0.7	0.08
7	6	UW	UD	1.4*	0.26
8	6	UW	UD	1.4*	0.19

[a] W=weighted D=dyed UW=unweighted UD=undyed
*statistically significant change determined by Duncan's Multiple Range Test (α=0.05)

specimens exhibited a negligible change in colour; for example, the colour changes for fabrics 1, 7, and 8, although statistically significant were barely perceptible, if at all. Billmeyer and Saltzman (1981) state that colour differences below 1 ΔE unit of change are not visible. The visible colour change which occurred for fabrics 2, 3 and 4 was in the form of an iridescent sheen. These fabrics were black, turquoise and maroon in colour, all dark or intense hues. All three also had compact weaves, and smooth or shiny surfaces. The change in appearance was due to interference bands which are caused by a slight variation in coating thickness on surfaces which are difficult for the gaseous monomer to penetrate (Humphrey, 1990). This effect has been observed by Grattan (1990) on silk textiles with shiny surfaces, and by Humphrey

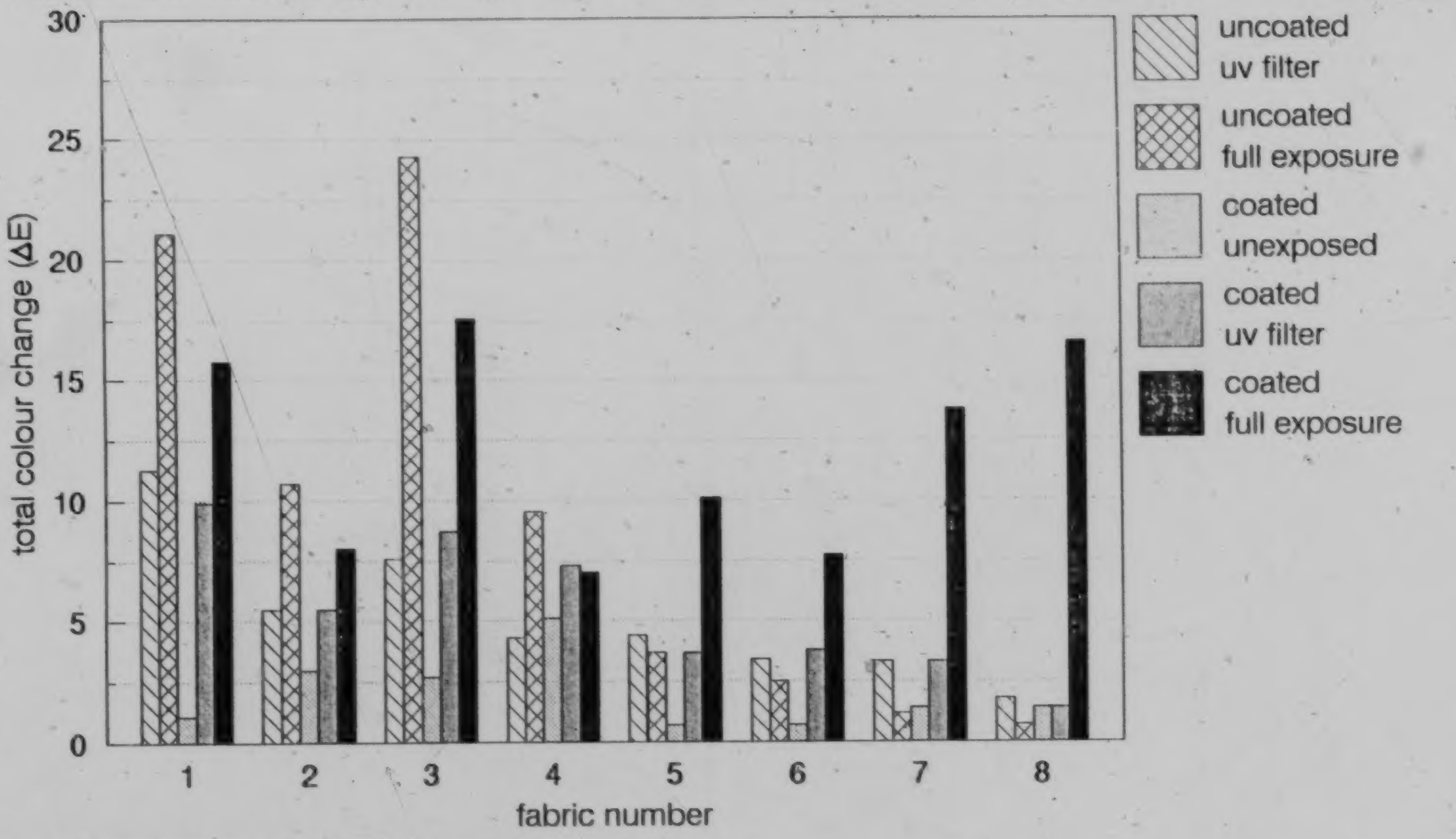
(1990) on coloured plates in books, which are often printed on smooth glossy paper. The appearance of interference bands is an inherent property for all types of thin transparent films, so is not unique to parylene. They disappear when the thickness of the coating is increased (Grattan, 1990; Humphrey, 1990).

As revealed in Figure 4 and Table 9, the dyed and undyed fabrics reacted differently when exposed to the xenon-arc lamp. The dyed fabrics exhibited distinct fading even when the UV component of the light had been filtered out; irradiation with wave-lengths in the visible region of the spectrum had sufficient energy to fade the dyes considerably. The colour change for coated and uncoated dyed fabrics was essentially the same. When samples were exposed to the xenon arc spectrum without a UV filter, however, the colour of the coated specimens changed less than the uncoated specimens if the fabric was dyed. For example, the uncoated fabric 3 faded from a brilliant turquoise to grey, a total change of 24.3 Colour Difference Units (CDU). Coated specimens of the same fabric also faded noticeably, but the overall colour difference was less (15.7 CDU). In contrast, the coated white specimens exhibited a larger change in colour than uncoated white specimens, as is illustrated by fabric 7: the coated specimens exhibited a visible colour change of 13.8 CDU due to yellowing, whereas the uncoated specimens exhibited a negligible change of 1.2 CDU.

In the CIElab* colour measurement system, the b* coordinate defines the yellowness (+b*) or blueness (-b*) of a material. Evaluation of the changes in the b* coordinate of the fabrics revealed that after full exposure, the b* values of the coated coloured specimens increased less than the b* values for the coated white specimens. Surprisingly, these values for two of the four coated dyed specimens showed they actually yellowed less than their uncoated counterparts. Upon visual inspection however, the faded coated specimens appeared

Figure 4

Total Colour Change (ΔE) of Parylene C-Coated Silk Fabric After Exposure to Simulated Daylight



Note. Samples were compared to the uncoated unexposed control sample, which had a ΔE = 0.

Table 9
Change in Colour (ΔE[a] and YI[b]) of Silk Fabrics After Exposure to Simulated Daylight

Fabric		Uncoated				Coated			
		UV filter[c]		Full[d]		UV filter		Full	
#	f[e]	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI
1	W D	11.3*	-	21.1*	-	9.6*	-	16.0*	-
2	W D	5.5*	-	10.7*	-	5.8*	-	6.9*	-
3	W D	7.6*	-	24.3*	-	7.1*	-	15.7*	-
4	W D	4.3*	-	9.5*	-	3.1*	-	4.6*	-
5	W UD	4.4*	0.73*	3.7*	1.24*	3.9*	0.78*	10.0*	1.76*
6	UW UD	3.4*	0.74*	2.5*	0.86*	3.3*	0.71*	7.9*	1.75*
7	UW UD	3.3*	0.64*	1.2*	1.07*	3.1*	0.64*	13.8*	2.54*
8	UW UD	1.8*	0.72*	0.7*	0.93*	2.7*	0.73*	15.3*	2.35*

Note. n= 6 except for fabrics 1 and 5 where n=3
[a] total colour difference (unexposed control has ΔE=0)
[b] yellowness index: normalized data (unexposed control=1)
[c] wave-lengths below 400 nm excluded
[d] exposed to full simulated daylight spectrum (xenon arc lamp)
[e] fabric finish: W=weighted D=dyed UW=unweighted UD=undyed
* statistically significant change from control as determined by Duncan's Multiple Range Test ($\alpha=0.05$)

darker than their uncoated counterparts, but were not necessarily less yellow.

The uncoated white specimens showed minimal total colour change (ΔE) upon full exposure, whereas the coated specimens visibly yellowed, suggesting the parylene C polymer coating had undergone degradation. Fabric 5, a weighted crepe fabric exhibited the largest colour change (3.7 CDU) by a fully exposed uncoated white specimen. This change was far lower than the colour differences for the white specimens with the parylene C coating, which ranged from 8 to 15 CDU. These results correspond to the general trends observed by Hansen and Ginell (1989) on new undyed silk fabric, but were less extreme. For their research, uncoated specimens exhibited a colour change of 5 CDU and coated specimens 22 CDU due to yellowing after a 242 kJ/m^2 exposure. The same Weather-Ometer temperature and relative humidity parameters (50 °C and 65% RH) were used for both studies.

Free parylene C films (12 μm thick) have been shown to yellow upon exposure to light but only when ultraviolet light was present. Films protected by a UV filter which excluded wave-lengths below 400 nm did not change in colour (Hansen & Ginell, 1989). Similarly, the UV filtered, coated silk samples in the present study did not yellow. Grattan (1990) has hypothesized that with the use of very thin coatings, any yellowing which occurs might be undetectable. The thinly coated fabrics in the present study challenge this concept, as they showed considerable yellowing upon exposure to the full spectrum. The colour change due to yellowing of the undyed coated fabrics, ranging from 8 to 15 CDU, was readily seen.

For the undyed fabrics, a measurement of yellowness index (YI) was taken in addition to the measure of total colour difference, ΔE. This index quantifies the nature of the light-induced colour change for neutral coloured fabrics better than ΔE because it specifically measures yellowness/whiteness, but is not suitable for use on dyed fabrics. The YI values for fabrics 5 to 8 are summarized in Table 9. The table shows that normalized YI values for specimens exposed to UV filtered light range from 0.64 to 0.74 for uncoated fabrics and from 0.64 to 0.78 for coated fabrics. This drop in YI of approximately 30% indicates that both the coated and uncoated specimens were bleached when exposure was limited to the visible spectrum. All the undyed fabrics were visually whiter after exposure to the UV filtered xenon arc light. Visible light is known to have a bleaching effect on wool, whereas ultraviolet light (below 365 nm) induces yellowing (Bendak, 1973; Launer, 1965a, b). The same behaviour was displayed by the undyed silk used in the present study. In research on the effect of visible light (wavelengths above 398 nm) on a variety of organic materials, Launer (1968) also demonstrated silk fabric to exhibit visible bleaching. In the present study, the uncoated, white specimens exposed to the full spectrum, which includes both ultraviolet and visible light, showed a negligible visual change in colour, possibly because bleaching and yellowing occurred in competition, simultaneously.

In general, the oxidation of polymers results in discolouration, or yellowing (Kamiya & Niki, 1978). The chemical mechanism by which silk yellows is uncertain. Researchers have postulated that the oxidation of specific amino acid residues, including tryptophan (Okamoto & Kimura, 1954), histidine and tyrosine (Inglis & Lennox, 1963) is responsible for the photoyellowing of wool and silk (Holt et al., 1977).

According to Maclaren and Milligan (1981) "Neither the chromophores responsible for the initial color of natural wool nor those produced by irradiation are known. Consequently little is known of the chemical changes responsible for photobleaching" (p. 227). Visible light does not have sufficient energy to break bonds, yet coloured structures are somehow removed, and the chromophores formed upon exposure to shorter more energetic wave-lengths are not produced (Bendak, 1978).

Flexural Rigidity

Flexural rigidity is a measure of fabric stiffness, calculated from the bending length and mass per unit area of the fabric. A 10% change in flexibility represents a just perceptible change in fabric hand (ASTM method: D1388-64). The parylene C coating produced a statistically significant (α=.05) initial increase in stiffness of all fabrics, as determined by the Duncan's Multiple Range Test (Table 10).

Table 10
Initial Effect of Parylene C Coating on the Flexural Rigidity of Silk Fabrics

Fabric # & finish[a]			Uncoated stiffness (mg-cm)	SD	Coated stiffness (mg-cm)	SD	Change in stiffness (%)
1	W	D	10.3	1.53	48.3	5.1	368*
2	W	D	13.4	3.62	42.9	19.2	220*
3	W	D	14.8	1.72	83.1	6.15	460*
4	W	D	29.7	1.99	185.8	28.89	524*
5	W	UD	12.7	0.78	55.3	6.22	336*
6	UW	UD	16.6	2.63	32.0	1.28	93*
7	UW	UD	24.2	3.64	64.7	5.27	167*
8	UW	UD	34.1	7.92	233.7	15.89	585*

Note. n= 10 except for fabrics 1 and 5 where n= 6
[a] W=weighted D=dyed UW=unweighted UD=undyed
* statistically significant change determined by Duncan's Multiple Range Test (α=0.05)

Those fabrics with compact weave structures showed the largest increase in flexural rigidity. Fabric 4, a tightly constructed plain weave increased in stiffness by 524%, while fabric 8, a compact twill weave increased 584%. Fabric 6 had a loose open construction and was least affected by the coating, showing an initial change of 92.9%. These results were in agreement with Grattan (1990) who noted the degree of change in flexibility was dependent on the weave structure.

In paper, the parylene coating forms contact bonds at the points where cellulose fibres cross one another, thus creating an overall strengthening effect (Humphrey, 1990). Plates 2, 4, and 5 in the subsequent section on Scanning Electron Microscopy illustrate that the coating performs the same function when applied to textiles. This action on textiles, however, prevents movement of fibres or yarns past one another, which reduces the ability of a fabric to drape. Because the yarns in tightly woven fabrics are packed closely together, there is an increased possibility of adjacent fibres becoming bonded together by the coating, thereby increasing stiffness.

The flexural rigidity measurements in mg-cm are listed in Appendix A-3 and illustrated by Figure 5. The changes in flexural rigidity for those specimens placed in the Weather-Ometer are summarized by the normalized data in Table 11. In all cases the flexibility did not change significantly

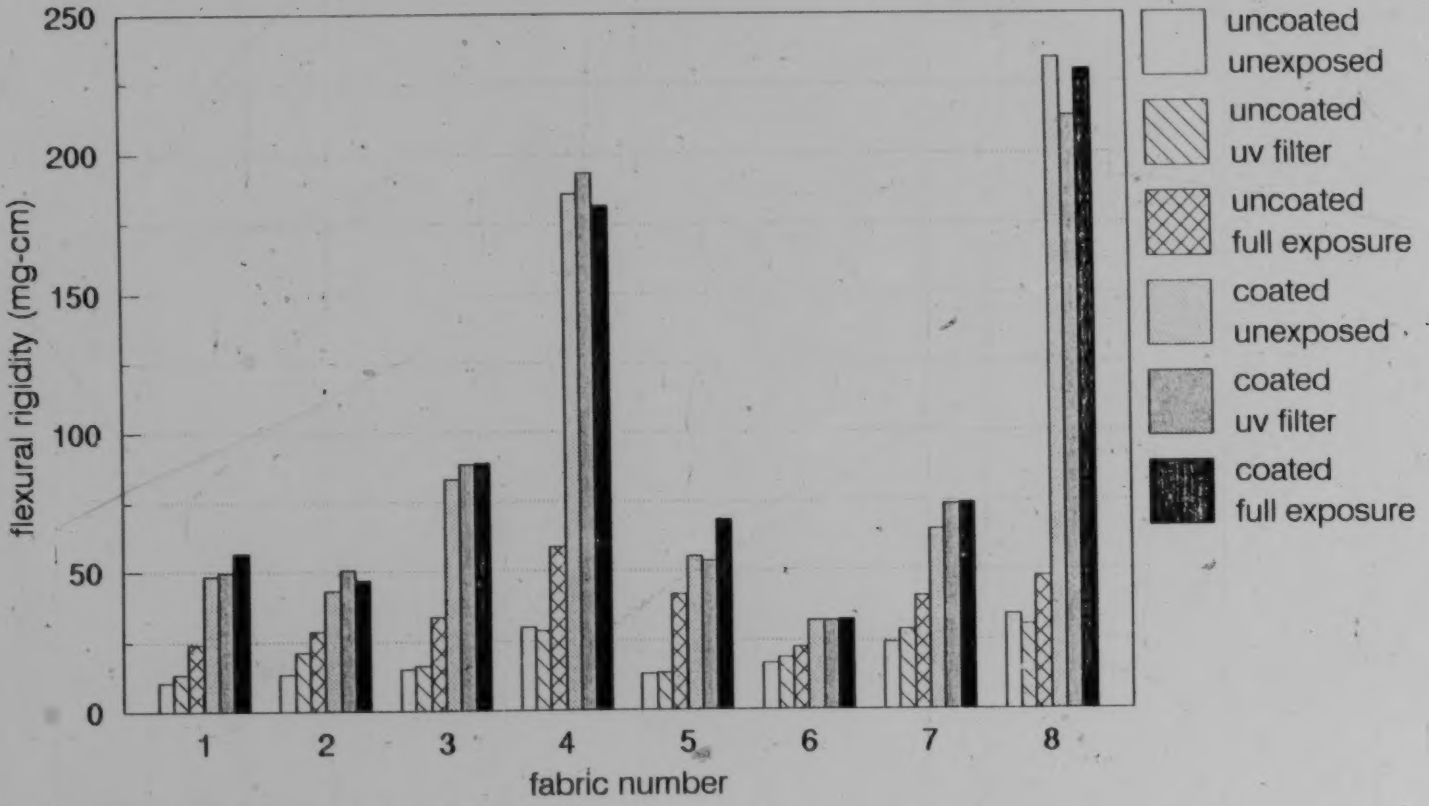
Table 11
Fraction of Flexural Rigidity Retained by Parylene C-Coated Silk Fabrics After Exposure to Simulated Daylight: Normalized Data[a]

Fabric # & finish[b]			Uncoated		Coated	
			UV filter[c]	Full[d]	UV filter	Full
1	W	D	1.31	2.34*	1.03	1.18
2	W	D	1.59	2.13*	1.17	1.09
3	W	D	0.07	2.28*	1.07	1.08
4	W	D	0.97	1.98*	1.04	0.98
5	W	UD	1.05	3.28*	0.97	1.24
6	UW	UD	1.13	1.36*	1.00	1.01
7	UW	UD	1.18	1.68*	1.14	1.14
8	UW	UD	0.89	1.40*	0.91	0.98

[a] uncoated unexposed control= 1 and coated unexposed control=1
[b] W=weighted D=dyed UW=unweighted UD=undyed
[c] wave-lengths below 400 nm excluded
[d] exposed to full simulated daylight spectrum (xenon arc lamp)
* statistically significant change from control as determined by Duncan's Multiple Range Test (α=0.05)

Figure 5

Flexural Rigidity of Parylene C-Coated Silk Fabric after Exposure to Simulated Daylight



Note. Samples were given 250 kJ of exposure in
a xenon arc Weather-Ometer with 65% relative
humidity and a black panel temperature of 50 °C

provided the specimens were protected from full irradiation by a UV filter. The uncoated specimens which were exposed to the full xenon-arc spectrum showed a statistically significant increase in flexural rigidity, with the weighted fabrics exhibiting more change than nonweighted. The most pronounced light-induced change in flexibility occurred with fabric 5, an undyed weighted crepe fabric, which became stiffer by 328% upon exposure. The chemical changes leading to increased embrittlement and stiffness are discussed in the section on extension.

The fabrics coated with parylene C were already more rigid than their uncoated counterparts before irradiation, but unlike the uncoated specimens, they did not exhibit a statistically significant change in flexibility upon full exposure to simulated daylight. Apparently, the exposure of 250 kJ/m^2 (420 nm) was not sufficient to reduce the flexibility of the parylene coating. Exposure to heat has been shown to cause embrittlement of free parylene films, as determined by failure to sustain a 180° bend test (Baker et al., 1980). Interestingly, the coating also appeared to keep the underlying silk from stiffening, because the parylene C-coated silk did not stiffen with exposure to light, whereas the uncoated silk did.

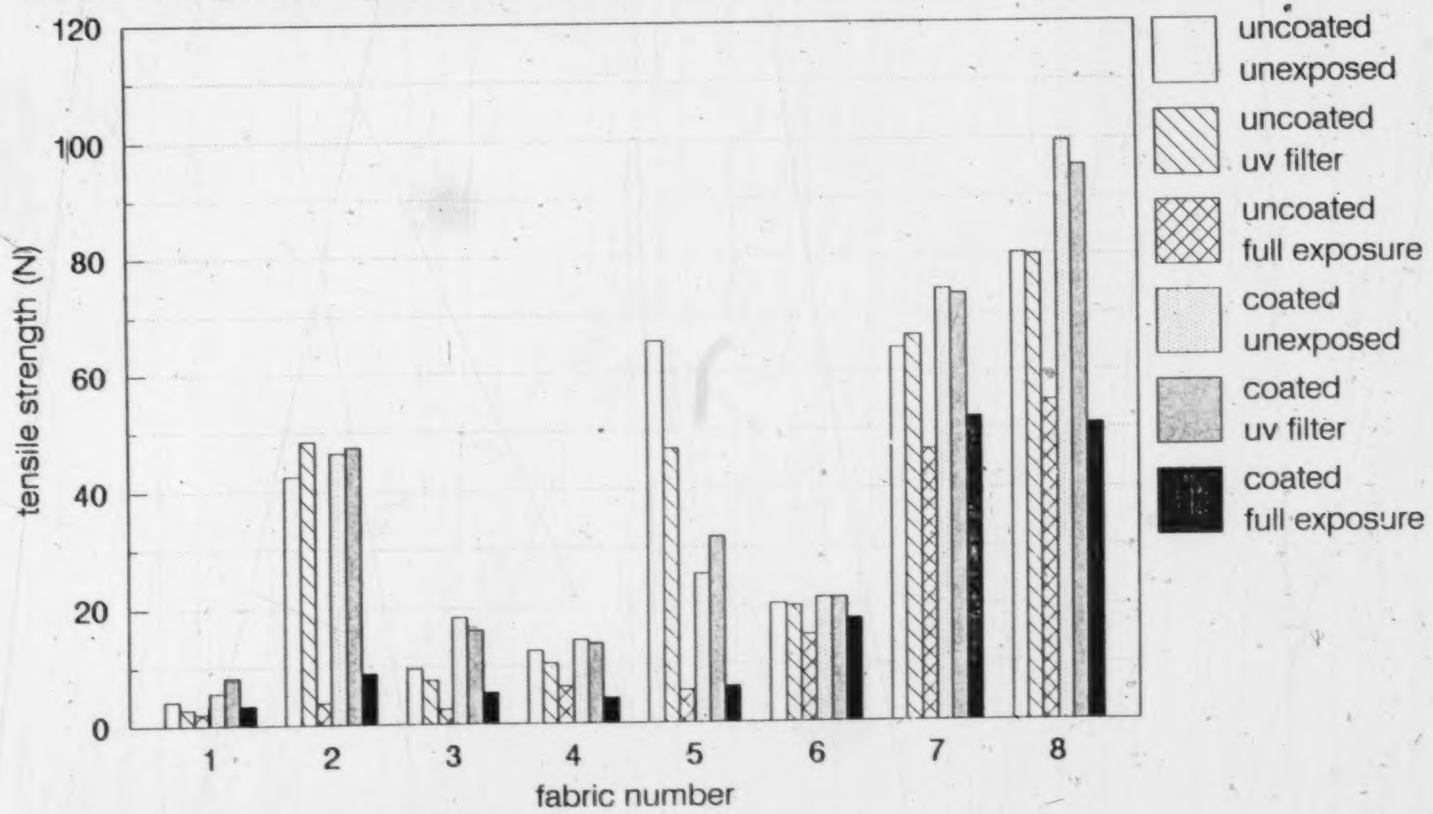
In summary, the results showed the coating initially caused a large increase in flexural rigidity; however, the uncoated specimens became stiffer with exposure to the full simulated daylight spectrum, while the coated specimens did not.

Tensile Properties

Tensile Strength

The effect of the coating on tensile strength for all fabrics is illustrated in Figure 6; further data from the strength tests is found in Appendix A-3. Although the parylene C coating produced an initial increase in tensile

Figure 6
Tensile Strength of Parylene C-Coated Silk Fabrics After Exposure to Simulated Daylight



Note. Samples were given 250 kJ of exposure in a xenon arc Weather-Ometer, with 65% relative humidity and a black panel temperature of 50 °C

Table 12

Initial Effect of Parylene C Coating on the Tensile Strength of Silk Fabrics

Fabric # & finish[a]			Uncoated strength (N)	SD	Coated strength (N)	SD	Change in strength (%)
1	W	D	4.12	1.85	5.15	1.58	+25.0
2	W	D	42.59	7.46	46.6	11.59	+9.4
3	W	D	9.50	6.66	18.32	5.40	+92.9
4	W	D	12.47	3.92	14.41	5.42	+15.6
5	W	UD	65.30	4.38	25.39	2.12	-61.1*
6	UW	UD	20.35	0.80	21.35	2.30	+4.9
7	UW	UD	64.02	5.07	74.11	8.98	+15.7*
8	UW	UD	80.22	3.56	99.46	6.84	+24.0*

Note. n= 10 except for fabrics 1 and 5 where n= 5

[a]W=weighted D=dyed UW=unweighted UD=undyed

* statistically significant change determined by Duncan's Multiple Range Test (α=0.05)

strength ranging from 5 to 24% for seven of the eight fabrics tested, the increase was only statistically significant for fabrics 7 and 8 as is shown in Table 12. The largest statistically significant increase was from 80.2 N to 99.5 N, or 24% for fabric 8, an artificially aged fabric which was initially stronger than the naturally aged specimens. Fabric 7, a naturally aged, unweighted, white fabric showed a significant initial increase in tensile strength of 15.7%, from 64 N to 74 N. Hansen and Ginell (1989) found the tensile strength of an undyed, unweighted naturally aged fabric to increase from 50 N to 64 N, a change of 28%. Their fabric received a thicker coating which may explain the higher increase in strength.

The application of the coating caused a statistically significant 61% loss in tensile strength for fabric 5. The weakening of this fabric may have been partly due to the high twist crepe yarns used in its construction. The coating may have caused this reduction in strength by bonding the fibres within the yarns to each other, thus reducing the fibres' ability to straighten and accommodate an applied force.

Fabrics 1 , 3, and 4, all coloured weighted fabrics, had the lowest tensile strength of the eight fabrics before coating. Although the parylene C coating produced an increase in their mean strength, this increase could not be established as statistically significant. As shown in Table 12, the standard deviation is very high when compared to the low mean of these three fabrics, making detection of statistically significant change difficult. Even the 93% increase in the mean strength for fabric 3 was not statistically significant because the coefficient of variation (100 SD/x) was over 70%. Nonetheless, it was readily apparent that these originally very fragile fabrics were more consolidated and thus easier to handle after application of the parylene C coating. Hansen and Ginell (1989) found a dyed and weighted silk fabric was strengthened by the parylene C coating, its tensile strength increasing from 32 N to 42 N, or 31%. Because the tensile strength values for the dyed and weighted fabrics in the present study were not statistically significant, a direct comparison to the numerical results of Hansen and Ginell could not be made.

Humphrey (1990) has observed that after the parylene coating was applied, weak papers exhibited a higher percentage increase in strength than initially strong papers. Research by Hansen and Ginell (1989) also showed fabrics which were initially strong and stable were the ones which received the largest absolute increase in tensile strength, but weak fabrics received a higher percent increase. The present study showed that the strongest fabrics initially (fabrics 5, 7, and 8) were the only three to show a statistically significant change in tensile strength. The largest percent increases in strength overall, however, were displayed by the weakest fabrics (fabrics 1 and 3) which saw increases in mean of 34% and 93% respectively;however, these changes in tensile strength were not statistically significant. If a larger sample size had been used for these fabrics, the high standard deviation which was responsible for the lack of statistical significance could have been reduced. In reference to his research on the consolidation of paper, Humphrey (1990) states that the parylene coating increases strength in two ways. It encapsulates each individual fibre in a consolidating sheath, thus producing an overall increase in strength. The coating also spot welds fibres together where they are in contact with one another, imparting greater stability. The same strengthening mechanism likely occurs for coated fabrics also.

The tensile strength of most coated and uncoated samples shielded by a UV filter during irradiation in the Weather-Ometer did not differ in a statistically significant way from the unexposed control specimens (Table 13). Both coated and uncoated specimens, however, exhibited loss in tensile strength after full exposure to the xenon-arc lamp. Among the five fabrics which saw a statistically significant light-induced decline in tensile strength, fabric 2, a black weighted satin, was the most severely affected: uncoated specimens retained only 9% of their original strength dropping from 42.6 N to 3.9 N, and the coated specimens retained 19%. The decline in strength for fabrics 1, 3, and 4 was not statistically significant due to the large variation within treatment groups.

After full exposure there was no statistically significant difference in the strength of coated and uncoated specimens, even for those fabrics which were initially strengthened. This trend is illustrated well by Figure 6, particularly for fabric 8. The bar graph shows the large initial increase in strength from 80.2 N to 99.5 N for fabric

Table 13
Fraction of Tensile Strength Retained by Parylene C-Coated Silk Fabrics After Exposure to Simulated Daylight: Normalized Data[a]

Fabric # & finish[b]			Uncoated		Coated	
			UV filter[c]	Full[d]	UV filter	Full
1	W	D	0.66	0.49	1.48	0.61
2	W	D	1.14	0.09*	1.01	0.19*
3	W	D	0.80	0.27	0.88	0.30*
4	W	D	0.82	0.51	0.96	0.31
5	W	UD	0.72*	0.08*	1.25	0.24*
6	UW	UD	0.98	0.73	1.00	0.83
7	UW	UD	1.03	0.73*	0.99	0.70*
8	UW	UD	0.99	0.68*	0.96	0.51*

[a] uncoated unexposed control=1 and coated unexposed control=1
[b] W=weighted D=dyed UW=unweighted UD=undyed
[c] wave-lengths below 400 nm excluded
[d] exposed to full simulated daylight spectrum (xenon arc lamp)
* statistically significant change from control as determined by Duncan's Multiple Range Test (α=0.05)

8. After exposure to the full simulated daylight spectrum, however, the strength of the uncoated specimens had declined to 54.9 N and the coated to 50.8 N, a difference which was not statistically significant. A similar experiment on parylene C-coated new silk fabric also showed the initial increase in strength after coating to be no longer apparent after full exposure to simulated daylight (Hansen and Ginell, 1989).

The tensile strength of silk fibres is known to be very sensitive to light. Nakanishi and Kobayashi (cited in Lucas et al, 1958, p. 189; Robson, 1985, p. 689) reported that exposure to light first caused breakage of hydrogen bonds, followed by photooxidation of the tyrosine residues. Through hydrolysis, water vapour then caused chain scission at the tyrosine residue. The resulting loss in degree of polymerization led to a decrease of tensile strength. The results of the present study suggested that high energy radiation in the ultraviolet region was required to initiate these reactions; when light of these wave-lengths was excluded by a UV filter, the drop in tensile strength after exposure to the remaining visible light rays was not statistically significant.

Even though parylene C is an excellent barrier to water vapour and other gases including oxygen, the coating was apparently incapable of slowing down the oxidative and hydrolytic reactions undergone by the silk substrate in this experiment. The parylene C polymer is known to be susceptible to oxidative degradation at high temperatures (Nowlin et al., 1980; Grattan & Bilz, 1991) and upon exposure to ultraviolet light (Beach et al., 1989) which causes embrittlement and loss of strength. An IR spectrum of a Parylene C film exposed to ultraviolet light revealed an increase in carbonyl content, indicating oxidation had occurred (Nova Tran, internal report). Conceivably, the coating's barrier properties are also reduced as it oxidizes, thus allowing the degradation of the underlying silk to occur at its normal rate.

Table 13 also shows that upon exposure to the full simulated daylight spectrum, weighted fabrics lost a greater percent of their initial strength than nonweighted. On average, weighted specimens retained 30% of their original strength, whereas nonweighted retained over 70%, regardless of coating. Weighted silk is highly sensitive to photooxidation, possibly due to its acidic nature (Becker et al, 1987). Because parylene C does not neutralize the acidity of weighted silk, these specimens would be expected to remain sensitive to light even after coating.

Extension at Break

The measurements for extension at break are listed in Appendix A-3, and presented diagrammatically in Figure 7. The only fabric to exhibit a statistically significant ($\alpha=0.05$) change after application of the parylene C coating was fabric 5 which lost of 53.4% of its original extension (Table 14). This crepe fabric originally had the highest extension of all the fabrics tested, possibly due to the highly twisted yarns which are largely responsible for the stretchiness of crepe fabrics. With coating application however, the fibres within the yarns likely became spot welded together, not allowing the yarns to shift and elongate when force was applied.

The extension of the remaining fabrics was not changed in

Table 14

Initial Effect of Parylene C Coating on the Extension at Break of Silk Fabrics

Fabric # & finish[a]			Uncoated extension (%)	SD	Coated extension (%)	SD	Change in extension (%)
1	W	D	2.17	0.43	1.41	0.35	-35.2
2	W	D	10.50	0.91	11.08	1.24	+5.53
3	W	D	3.22	0.95	3.30	0.91	+2.7
4	W	D	3.0	0.53	1.50	0.54	-50.0
5	W	UD	11.53	0.95	5.37	0.47	-53.4*
6	UW	UD	10.01	1.07	9.84	1.67	-1.66
7	UW	UD	11.44	1.02	12.10	2.00	+5.77
8	UW	UD	9.39	0.68	10.60	0.33	+12.84

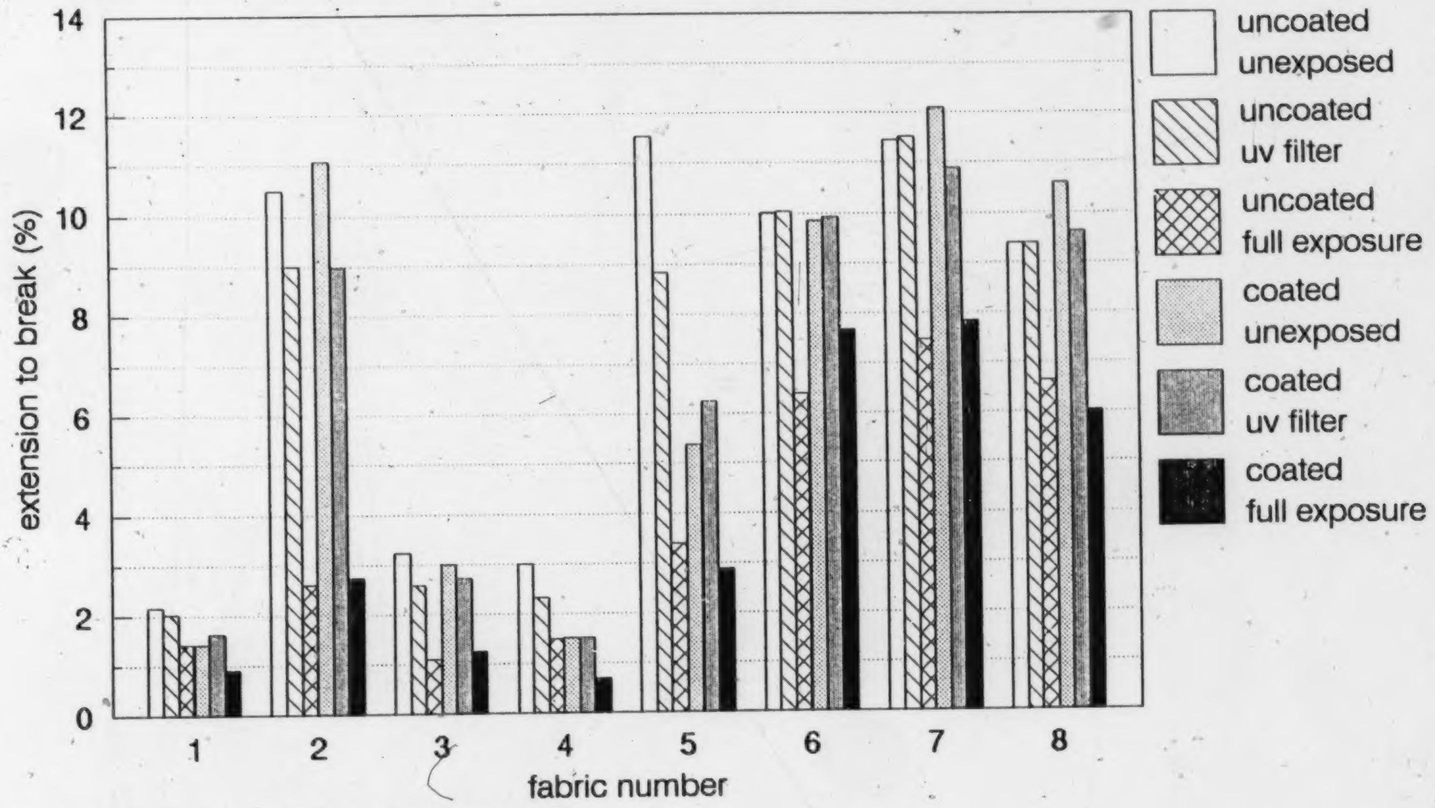
Note. n= 10 except for fabrics 1 and 5 where n= 5

[a] W=weighted D=dyed UW=unweighted UD=undyed

* statistically significant change determined by Duncan's Multiple Range Test ($\alpha=0.05$)

Figure 7

Extension to Break of Parylene C-Coated Silk Fabrics Exposed to Simulated Daylight



Note. Samples were given 250 kJ of exposure in a xenon arc Weather-Ometer, with 65% relative humidity and a black panel temperature of 50 °C

a statistically significant way by the addition of the parylene C coating. The change in extension for fabrics 2, 3, 6, and 7 was less than 6%, which was not large enough to be statistically significant given the standard deviations with the treatment groups. Fabrics 1 and 4 displayed high sample variability; the standard of deviations for these fabrics were high relative to the means causing their substantial drops in extension to be not statistically significant. These results are in general agreement with the observations of Hansen and Ginell (1989), who noted the extension for naturally aged silk fabrics to either remain unchanged or decline after coating. They found the coating to have a distinctly different effect on a modern, unaged fabric which increased in extension from 13.1% to 15.1%, an increase of 15%. They concluded that already embrittled silk did not become more extensible with a thin coating of parylene C. Similarly, Humphrey (1988) found that a thin layer of parylene did not always improve fold endurance of brittle paper. The coating can break along with the paper upon flexing if the ratio between paper thickness and coating thickness is too high. Performance in a fold endurance test gives an indication of the paper's extensibility because flexibility and extension are very closely related. In order for a fibre or film to bend, it must be capable of elongation on one side and compression on the other (Hearle, 1963b).

As shown in Table 15, exposure limited to the visible portion of the spectrum (above 400 nm) did not produce a statistically significant difference in extension for any of the coated or uncoated specimens, with the exception of fabric 5. The uncoated specimens for fabric 5, an undyed weighted fabric, showed a statistically significant 24% loss in extension, even when exposure was limited to visible light. The remaining seven fabrics exhibited statistically insignificant changes in extension, ranging from a 20% decrease for uncoated Fabric 3 to a 15% increase for coated

Table 15

Fraction of Extension at Break Retained by Silk Fabrics After Exposure to Simulated Daylight: Normalized Data[a]

Fabric # & finish[b]			Uncoated		Coated	
			UV filter[c]	Full[d]	UV filter	Full
1	W	D	0.93	0.65	1.15	0.65
2	W	D	0.85	0.25*	0.81	0.25*
3	W	D	0.80	0.34*	0.82	0.38*
4	W	D	0.77	0.45*	1.01	0.46
5	W	UD	0.76*	0.29*	1.17	0.53*
6	UW	UD	1.00	0.64*	1.01	0.78*
7	UW	UD	1.00	0.65*	0.90	0.65*
8	UW	UD	1.00	0.71*	0.91	0.57*

[a] uncoated unexposed control= 1 and coated unexposed control=1
[b] W=weighted D=dyed UW=unweighted UD=undyed
[c] wave-lengths below 400 nm excluded
[d] exposed to full simulated daylight spectrum (xenon arc lamp)
* statistically significant change from control as determined by Duncan's Multiple Range Test (α=0.05)

fabric 1. The average 18% drop in extension displayed by the uncoated weighted fabrics as a group, however, was greater (statistically significant as determined by Duncan's Multiple Range Test) than the loss exhibited by the nonweighted fabrics. Parylene C-coated fabrics for both weighted and nonweighted specimens lost an average of only 5% of their original extension at break.

For six of the fabrics (fabrics 2, 3, 5, 6, 7, and 8) exposure to the full simulated solar spectrum resulted in a statistically significant decline in extension for both coated and uncoated specimens as shown in Table 15 and Figure 6. After full exposure to the xenon arc lamp, these fabrics retained from 25% to 78% of their original extension at break.

The extension of a black weighted satin (fabric 2) showed the largest decline, with both coated and uncoated specimens retaining only 25% of their original extension. Weighted fabrics lost a larger percentage of their initial extension than did nonweighted upon exposure to the full simulated solar spectrum. On average, weighted specimens retained about 40% of their original extensibility whereas nonweighted retained 67%.

Fabric 6 was the only case where there was a significant difference between coated and uncoated specimens after exposure to the full simulated solar spectrum. In this one instance, there was no initial increase in extension, but after full exposure the uncoated specimens displayed an extension at break of 6.4% while the coated specimens had a higher extension of 7.7%. For the remaining seven fabrics, there was no statistically significant difference between the extensions of the coated and the uncoated specimens after exposure to the full simulated daylight spectrum.

A fibre or polymer loses its extensibility when the molecules in the amorphous regions are no longer free to slide past one another when a load is applied. Increased orientation or increased crystallinity can both lead to less extensibility. Research by Tsukada and Hirabayashi (1980), however, showed the crystallinity of UV-exposed silk to remain unchanged while orientation decreased slightly. The formation of cross-links can also increase the brittleness of a material by inhibiting the movement of the molecular chains. Schnabel and Kiwi (1978) assert, however, that for polymers susceptible to autoxidation, light-induced cross-linking only occurs in the absence of oxygen. When oxygen is present autoxidation occurs, which increases the rate of main chain scission and prevents cross-linking. They continue on to say the photooxidation mechanism itself eventually causes an increase in stiffness and embrittlement in addition to discolouration and loss in strength.

According to Nakanishi and Kobayashi (cited in Lucas et al., 1958, p. 189; Robson, 1985, p. 689) light induces oxidation of the tyrosine amino acid residue and subsequent hydrolytic chain scission at this residue. Because tyrosine is a bulky aromatic amino acid, it is likely located in the amorphous regions of fibroin. If chain scission were confined to the amorphous regions of the fibre, these regions would gradually erode away, leading to an eventual loss in extension. Okamoto (cited in Lucas et al, 1958,p. 189; Robson, 1985, p.688) concluded photochemical damage was most rapid in the amorphous regions, with tyrosine, threonine and leucine being most affected. Amino acid analysis by Miller (1986) showed decreases in the amounts of proline, valine, methionine, isoleucine, phenylalanine and lysine after exposure to 80 AATCC Fading Units (AFU) of xenon-arc simulated daylight. All of these residues contain long side chains, leading Miller to conclude her experimental treatment had primarily affected the amorphous regions.

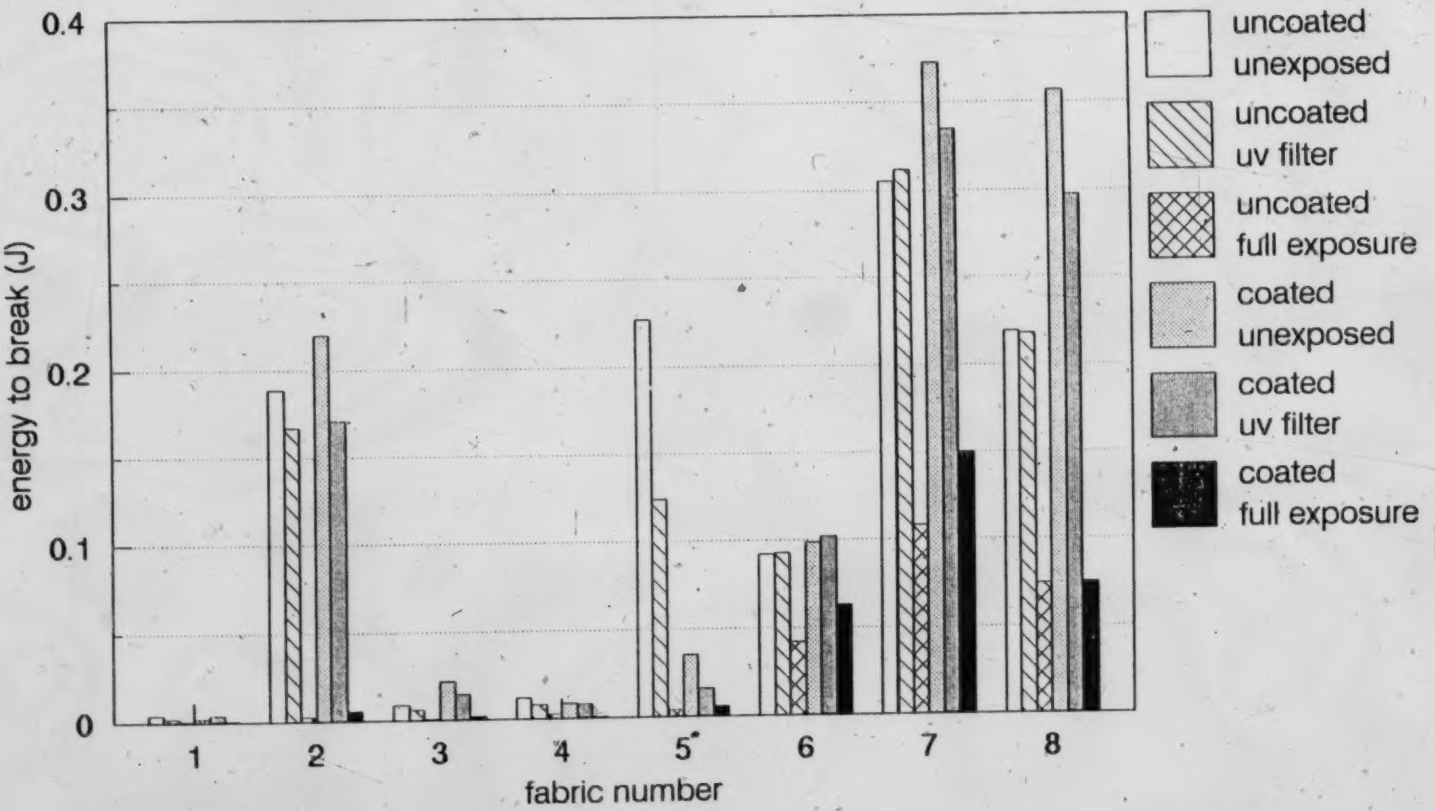
In a study of fibre fractures, Bresee & Goodyear (1986) concluded that naturally aged silk did not exhibit increased brittleness because of the low number of brittle-type fractures present. Rather, a loss of interfibrillar cohesion was cited as the main cause of deterioration. Dobb et al. (1967) proposed that the microfibrils comprise the crystalline ß-structure portion of fibroin, and the amorphous regions occupy the space between the fibrils. If these amorphous regions are gradually reduced through repeated chain scission, loss of cohesion between the microfibrils may result.

Energy to Break

Energy to break, or work of rupture, is a measure of the overall toughness of a fabric, taking both extension and tensile strength into account. Figure 8 illustrates the effects of the coating and exposure on each of the fabrics tested, and a list of the energy to break values (J) for each

Figure 8

Energy to Break of Parylene C Coated Silk Fabric After Exposure to Simulated Daylight



* Note. Samples were given 250 kJ of exposure in a xenon arc Weather-Ometer, with 65% relative humidity and a black panel temperature of 50 °C

treatment group is given in Appendix A-3. Table 16 shows the initial effects of the coating on the energy to break of the eight silk fabrics. The addition of parylene C significantly increased the initial energy to break for fabric 7 and fabric 8. Fabric 7 was a naturally aged, light-weight, white silk lining fabric with a plain weave, and fabric 8 was an artificially aged, heavier undyed fabric with a twill weave. Both fabrics were relatively strong and stable before the parylene C coating was applied. The work of rupture for the three weakest fabrics, fabrics 1, 3, and 4, was not significantly ($\alpha=0.05$) improved by the coating due to the extreme variability of the specimens; for example, the energy to break for fabric 3 showed a 144% increase after application

Table 16
Initial Effect of Parylene C Coating on the Energy to Break of Silk Fabrics

Fabric # & finish[a]			Uncoated energy (J)	SD	Coated energy (J)	SD	Change in energy (%)
1	W	D	0.004	0.003	0.002	0.001	-50.0
2	W	D	0.189	0.056	0.220	0.075	+16.4
3	W	D	0.009	0.009	0.022	0.010	+144.4
4	W	D	0.012	0.006	0.009	0.007	-25.0
5	W	UD	0.227	0.045	0.035	0.006	-84.6*
6	UW	UD	0.092	0.012	0.099	0.029	+7.6
7	UW	UD	0.305	0.047	0.373	0.121	+22.3*
8	UW	UD	0.219	0.031	0.357	0.041	+63.0*

Note. n= 10 except for fabrics 1 and 5 where n= 5
[a] W=weighted D=dyed UW=unweighted UD=undyed
* statistically significant change determined by Duncan's Multiple Range Test ($\alpha=0.05$)

of the coating, yet this change was not statistically significant. As shown in Table 16, the standard deviation was very high compared to the mean for fabric 3; the mean of the uncoated specimens was 0.009 J, and the standard deviation was also 0.009 J, giving a coefficient of variation of 100%. Fabric 5 exhibited a noticeable loss of energy at break, which was not surprising because this fabric also had exhibited a large loss in tensile strength and extension, the combination of which resulted in its loss of energy to break.

The unweighted, undyed naturally aged fabric studied by Hansen and Ginell (1989) increased in energy to break from 0.192 J to 0.213 J, or 10.9% upon the application of a 1 μm coating of parylene C. Fabric 7, also an undyed, unweighted fabric, reacted in a similar manner displaying a 22.3% increase with a 0.6 μm coating. The dyed, weighted fabric used by Hansen and Ginell (1989) also showed an increase from 0.041 J to 0.049 J, a change of 19.5%. Results from the present study showed the change in energy to break for weighted, dyed specimens was extremely variable and not statistically significant.

The very weak fabrics (fabrics 1, 3 and 4) whose work of rupture was not altered significantly by application of the coating were not changed by light exposure either (Table 17) Again, the variation within treatment groups for these fabrics was high making a statistically significant loss difficult to identify. Fabric 4, for example, retained only 25% of its original energy to break when uncoated, and 11% when coated. Even though this loss was considerable, it was still not statistically significant given the relatively high standard deviation. If a larger number of specimens had been used, this variability may have been reduced. Fabric 2, a weighted black satin, experienced the greatest statistically significant drop in work of rupture with coated and uncoated specimens retaining only 2% and 3% of their original energy to break respectively.

Table 17
Fraction of Energy to Break Retained by Silk Fabrics After Exposure to Simulated Daylight: Normalized Data[a]

fabric # & finish[b]			uncoated		coated	
			UV filter[c]	full[d]	UV filter	full
1	W	D	0.54	0.22	1.84	0.33
2	W	D	0.88	0.02*	0.78	0.03*
3	W	D	0.67	0.08	0.68	0.09
4	W	D	0.67	0.25	0.89	0.11
5	W	UD	0.55*	0.02*	0.46	0.17
6	UW	UD	1.01	0.46	1.03	0.63
7	UW	UD	1.02	0.35*	0.90	0.40*
8	UW	UD	1.00	0.34*	0.83*	0.21*

Note. n= 10 except for fabrics 1 and 5 where n=5
[a] uncoated unexposed control= 1 and coated unexposed control=1
[b] W=weighted D=dyed UW=unweighted UD=undyed
[c] wave-lengths below 400 nm excluded
[d] exposed to full simulated daylight spectrum (xenon arc lamp)
* statistically significant change from control as determined by Duncan's Multiple Range Test (α=0.05)

For fabrics which were initially influenced by the parylene C coating (fabrics 5, 7 and 8), the UV-filtered samples were not significantly different from the unexposed control samples. The coated samples retained a higher energy to break than the uncoated samples for fabrics 7 and 8, when the UV light was filtered out. For example, the bar graph (Figure 7) shows for fabric 7 an initial increase in energy to break, from 0.31 J to 0.37 J, after coating. After exposure to UV-filtered xenon arc light, the energy to break for both coated and uncoated samples changed slightly, but the coated sample still had a higher energy to break than the uncoated (0.34 J vs 0.31 J).

In all cases, the energy to break dropped upon exposure to the full simulated daylight spectrum until there was no longer a significant difference between coated and uncoated samples. The energy to break for fabric 7 dropped to 0.15 J for parylene C-coated samples, and 0.11 J for uncoated samples, but the difference between the two was not statistically significant.

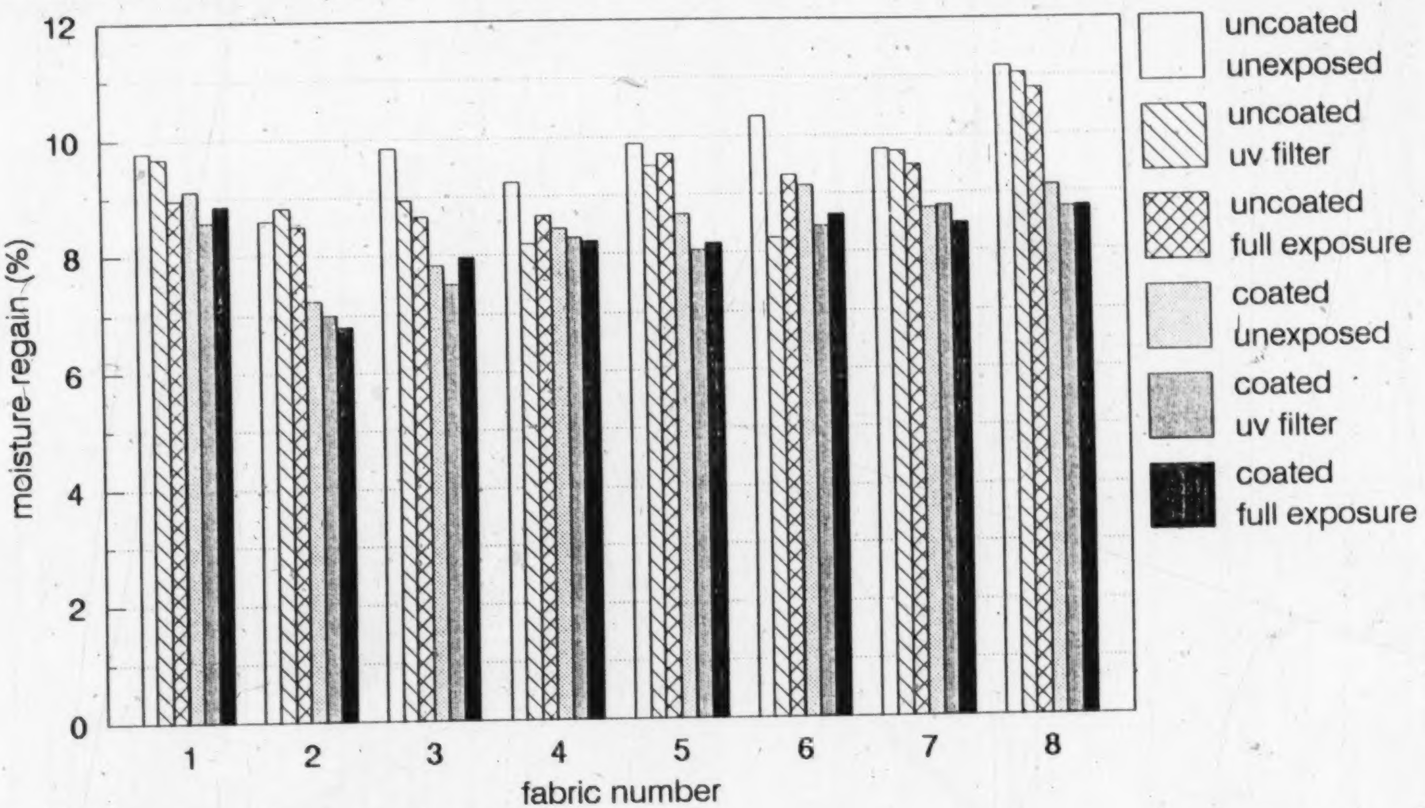
Weighted fabrics lost more energy to break upon full exposure than did nonweighted, with coated and uncoated fabrics changing in the same way. Weighted specimens retained only about 12.5% of their initial work of rupture after full exposure, whereas nonweighted retained 40%.

Moisture Regain

The moisture regain values (%) for each of the eight fabrics tested are presented in Appendix A-3, and represented diagrammatically by Figure 9. Application of the parylene C coating caused a decrease in the moisture regain of all fabrics, as shown in Table 18. Fabric 1 was least affected by the coating, its moisture regain only dropping from 9.78% to 9.12%, a statistically insignificant decline of 6.7%. All other fabrics showed a significant change in moisture regain with the addition of parylene C, the largest being exhibited by fabric 3, which dropped from 9.83% to 7.82%, a change of 20.4%.

Even though the moisture regain of the coated samples appeared to drop, the actual amount of water vapour absorbed by the fabric substrate was likely unchanged. The parylene C coating increased the mass per unit area of the specimens, yet was not in itself capable of absorbing water vapour; therefore, if the silk fabric beneath the coating absorbed the same amount of water vapour as the uncoated fabric, the moisture regain calculated for the coated specimen would be less than the uncoated specimen because of the increase in initial mass of the coated specimen. The relationship between

Figure 9
Moisture Regain of Parylene C-Coated Silk Fabric After Exposure to Simulated Daylight



Note. Samples were given 250 kJ of exposure in a xenon arc Weather-Ometer, with 65% relative humidity and a black panel temperature of 50 °C

Table 18

Initial Effect of Parylene C Coating on the Moisture Regain of Silk Fabrics

Fabric # & finish[a]			Uncoated regain (%)	SD	Coated regain (%)	SD	Change in regain (%)
1	W	D	9.78	0.76	9.12	0.85	6.7
2	W	D	8.61	0.27	7.23	0.43	16.0*
3	W	D	9.83	0.51	7.82	0.63	20.4*
4	W	D	9.23	0.45	8.45	0.18	8.4*
5	W	UD	9.88	0.45	8.67	0.05	12.3*
6	UW	UD	10.33	0.76	9.04	0.51	12.5*
7	UW	UD	9.75	0.50	8.75	0.11	10.3*
8	UW	UD	11.17	0.19	9.11	0.22	18.5*

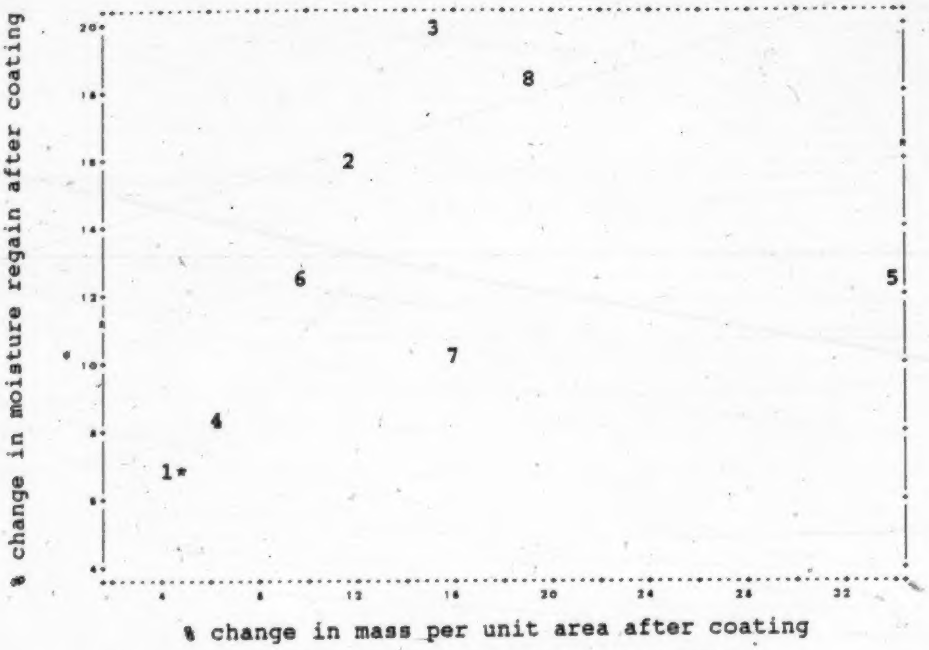
Note. n=3

[a] W=weighted D=dyed UW=unweighted UD=undyed

* statistically significant change determined by Duncan's Multiple Range Test ($\alpha=0.05$)

the change in moisture regain and the change in mass per unit area is illustrated by Figure 10. The scattergram shows that generally, the larger the increase in mass due to the coating, the greater the drop in moisture regain. The correlation between these two variables (r=0.33) is not as strong as expected because the point for fabric 5 falls outside the general trend.

Parylene C is known to have an extremely low permeability for atmospheric moisture (Loeb, 1971), meaning that the coating is not completely impervious to water vapour, but transmits it very slowly. The results from the moisture regain tests in this study suggest that the silk fabrics absorbed similar amounts of moisture both before and after



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          8 cases plotted. Regression statistics of DMR on DMASS:
Correlation   .32868 R Squared   .10804  S.E. of Est    4.91862  2-tailed Sig.   .4267
Intercept(S.E.)   10.70182(  3.34498)  Slope(S.E.)  .18884(   .18571)
```

* fabric #

Figure 10. Relationship between change in mass per unit area and change in moisture regain, after coating application.

coating with parylene C, indicating the coating is permeable to water vapour. Two days of exposure to humid conditions was sufficient for both the coated and uncoated specimens to equilibrate, but it is likely the uncoated specimens equilibrated more quickly than those coated with the parylene C polymer.

The moisture regain for all the coated specimens, and the uncoated specimens for fabrics 2, 5, 7, and 8 remained constant after exposure to simulated daylight, as shown in Table 19 and Figure 9. The remaining uncoated samples (fabrics 1, 3, 4 and 6) exhibited change upon exposure to light. The effect was slightly different for each fabric, but generally, the moisture regain decreased no more than 20% for the UV filtered and/or fully exposed samples. For fabrics 1, 4, and 6, the light-induced drop in moisture regain was sufficient for there no longer to be a significant difference

Table 19

Fraction of Moisture Regain Retained by Silk Fabrics After Exposure to Simulated Daylight: Normalized Data[a]

fabric # & finish[b]			uncoated		coated	
			UV filter[c]	full[d]	UV filter	full
1	W	D	0.99	0.92*	0.94	0.97
2	W	D	1.02	0.99	0.97	0.94
3	W	D	0.91*	0.88*	0.96	1.02
4	W	D	0.89*	0.94	0.97	0.97
5	W	UD	0.96	0.98	0.92	0.94
6	UW	UD	0.80*	0.90*	0.93	0.96
7	UW	UD	1.0	0.97	1.0	0.97
8	UW	UD	0.99	0.97	0.96	0.96

Note. n= 3

[a] uncoated control= 1 and coated control= 1

[b] W=weighted D=dyed UW=unweighted UD=undyed

[c] wave-lengths below 400 nm excluded

[d] exposed to full simulated daylight spectrum (xenon arc lamp)

* statistically significant change from control as determined by Duncan's Multiple Range Test (α=0.05)

between the uncoated and the coated samples. As shown in Figure 9, for example, fabric 4 dropped in moisture regain from 9.2% to 8.2% after exposure to UV-filtered xenon arc light. The moisture regain for the coated samples remained at about 8.3%, as these samples were not significantly affected by exposure to light; the difference between 8.2% and 8.3% was not statistically significant.

There was no apparent association between the type of fabric and the effect of the coating on moisture regain. The presence of weighting agents, dye, or whether the fabric had been naturally or artificially aged all had no statistically significant effect.

Scanning Electron Microscopy

The fibres shown in Plate 1 are typical of the uncoated silk fibres seen in the fabrics analyzed by scanning electron microscopy. Some fibres were smooth and regular, while others were more damaged, with fibrils peeling away from the surface of the fibre. At magnifications of 1000x, the parylene C coating was highly conformal, and was imperceptible on the smooth, undamaged fibres as seen in the lower left corner of Plate 2. The coating appears more obvious on the fibres in the centre of Plate 2, which likely had surface irregularities prior to coating, created by fibrillation or the presence of surface debris. Whenever a fibril had separated from the shaft of the fibre, the individual fibrils were coated making them appear much thicker, as depicted in Plates 4 and 5. These plates also show how these loose fibrils can become bonded across neighbouring fibres by the coating. These bridges would restrict movement of fibres past one another, providing a partial explanation for the increase in stiffness displayed by coated fabrics. In areas where fibres were very close together, they were occasionally bonded directly to each other (Plates 2, 5, and 7), thus decreasing flexibility and possibly extension.

The presence of surface debris before application may also have a large effect on the appearance of the coating. The artificially aged fabric 8 appeared to have debris on its surface before coating (Plate 3) which may have been responsible for the very 'globby' irregular appearance of the coated surface of this fabric (Plate 4). The surface of a coated specimen from fabric 8, depicted by Plate 4, is seen to contrasts highly with the smooth appearance of the coating on some of the fibres in Plate 2.

The surface debris apparent on fabric 8 may have been deposited during the artificial aging process in the Weather-Ometer. During the aging procedure, a noticeable film formed on all exposed surfaces within the chamber, and was most obvious on the clear borosilicate filter over the xenon arc burner. A deposit similar to that on fabric 8 was seen only on the fully exposed naturally aged specimens. These specimens were the only ones directly exposed within the chamber, as the other treatment groups were covered by masks or film.

As shown by Plates 6 and 7, the coating appears to have become embrittled upon exposure to the full daylight spectrum. Because the SEM specimens were cut from strips originally used to perform tensile strength tests, the fibres examined may have had strain applied to them. On fully exposed specimens of fabrics 5, 7, and 8 cracking was evident. This behaviour was limited to the fully exposed coated samples. A UV filtered coated specimen deliberately taken close to the stress-induced rupture of fabric did not exhibit cracking. Also, the damage was primarily apparent on fibres lying in one direction, this likely being the direction in which the breaking force was applied. The combination of these observations suggests both strain and exposure to the full xenon arc spectrum were jointly responsible for the cracked appearance of the coated fibres.

Energy Dispersive X-Ray Analysis (EDXA) was performed on some of the fabrics. Fabric 2, a black weighted satin showed a large amount of tin present due to the tin salts used in the weighting of this fabric. The chlorine component of parylene C was also detected when this technique was applied to the coated fabrics.

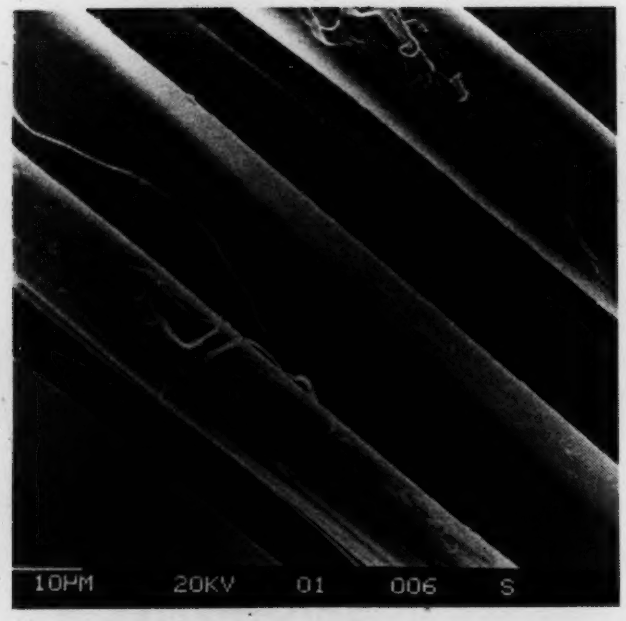
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Plate 1. Combination of undamaged and fibrillated fibres in uncoated fabric 2 after exposure to UV-filtered light (1000x).

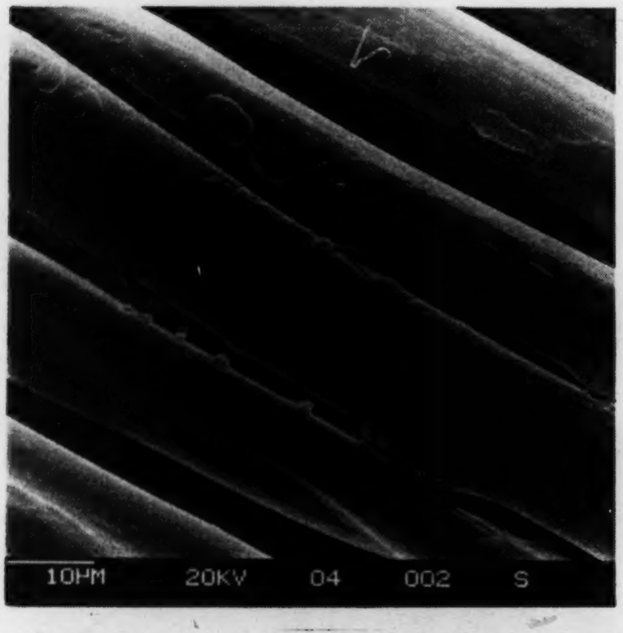
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Plate 2. Parylene C-coated fabric 2 before exposure to light showing smooth coating on some fibres, irregular on others depending on state of fibre surface prior to coating (1000x).

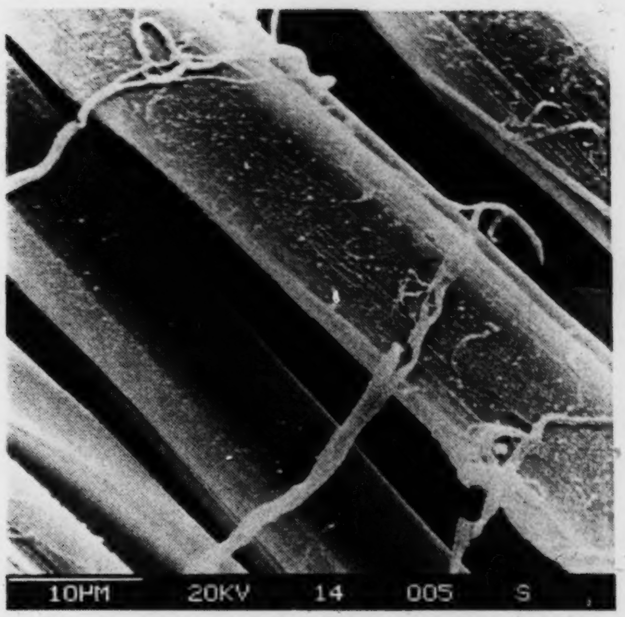

Plate 3. Overall surface debris, and fibrils extending across neighbouring fibres on uncoated fabric 8 exposed to UV-filtered light (1600x).

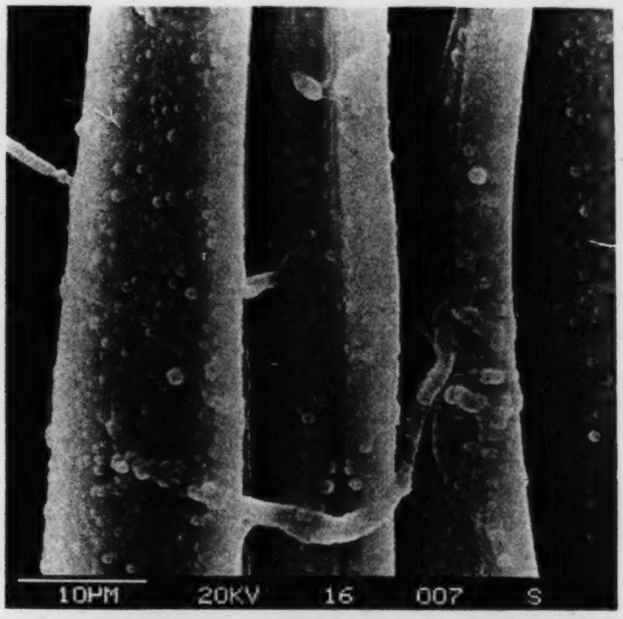

Plate 4. Thickened fibrils bonded to neighbouring fibres, and irregular coated surface due to underlying debris on coated fabric 8 exposed to UV-filtered light (1500x).

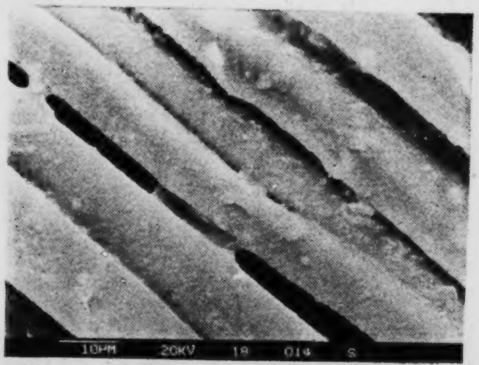

Plate 5. Coated fibres bonded together (spot welded), and debris on coated fibre surface of fabric 5 after exposure to the full simulated daylight spectrum (1500x).

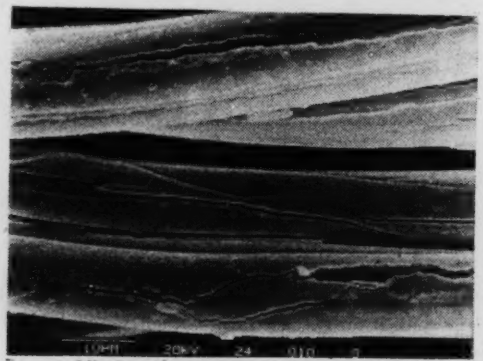

Plate 6. Cracking of parylene C coating on fabric 8 after exposure to the full xenon arc spectrum and stress (1500x).

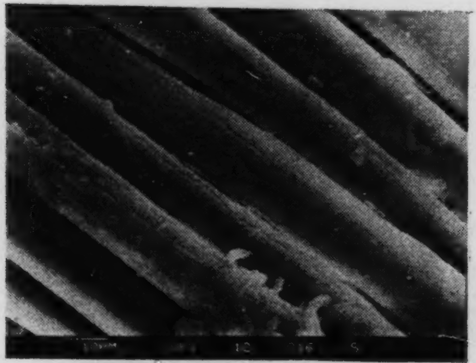

Plate 7. Coated fibrils forming bridges between fibres, and cracking of parylene coating on fabric 7 after exposure to the full xenon arc spectrum and stress (1000x).

Summary of Results

Like most conservation treatments, the parylene coating technology has both advantages and shortcomings. The polymer is effective in providing overall consolidation of fragile fabrics which minimizes the potential for further damage through handling. Parylene's unique gas-phase deposition process provides a protective conformal coating to all surfaces down to the smallest fibril. This strengthening mechanism, however, noticeably reduces the flexibility of fabrics and the appearance of some fabrics can also be altered slightly. These shortcomings, however, may not be of primary importance in cases where severely degraded artifacts require consolidation merely to remain intact. It is in these extreme cases where parylene C may prove to be the most useful.

The effect of the parylene C polymer on the properties of eight varied silk fabrics, and the performance of the coating upon exposure to a simulated daylight spectrum, are discussed below.

Initial Effect of Parylene C Coating

The initial effect of a parylene C coating less than 1 μm thick on silk fabric properties was largely dependent on fabric structure. This study showed those fabrics which were compactly woven, with shiny surfaces and dark dyes experienced a change in appearance arising from the formation of rainbow-like interference bands. Silk textiles containing dark-coloured dyes are frequently among the most degraded in textile collections; however, if the coating were able to impart additional strength to ensure safer handling of such artifacts, this change in appearance might be acceptable. In addition, the interference bands will disappear if the coating thickness is increased (Grattan, 1990; Humphrey, 1990), which in turn would reduce flexibility.

Even when a coating less than 1 μm thick was used, those fabrics with tightly constructed, compact weaves (fabrics 3, 4 and 8) exhibited a noticeable stiffening of hand, as reflected by the 4 fold increase in flexural rigidity. Fabric 6 had a more open structure and showed the least change in flexural rigidity, but was still noticeably stiffer. SEM analysis revealed that adjacent fibres were sometimes bonded together by the parylene C coating. In addition, tiny fibrils which had peeled away from fibre surfaces became spot-welded to neighbouring fibres by the coating. These occurrences inhibit fibre movement and adversely affect flexibility; however, a change in flexibility may not be of primary importance if a disintegrating artifact needs consolidation to keep it from falling apart entirely.

Although the bonding of fibres may be responsible for the decreased flexibility of the fabrics, it is also the mechanism by which the parylene C polymer strengthens and consolidates the fabric. The initial effect of the coating on tensile properties was difficult to evaluate because the naturally aged specimens displayed a large variation in properties within treatment groups. Obvious fabric splits and holes were avoided in cutting the individual specimens, but some fabrics still must have had some sections which were substantially weaker than others. Even though some parylene C-treated samples had a large percent increase in tensile strength as determined by Instron testing, this difference was not shown to be statistically significant. Such was the case with fabrics 1, 3 and 4 which were badly degraded and were most representative of fabric which might be considered for parylene treatment. Subjectively however, the fabric panels were found to be easier to handle after application of parylene C, their splits and weak areas being consolidated.

Generally, the coating produced an increase in tensile strength and energy to break which would allow delicate artifacts to be manipulated more safely. An increase in extension was not apparent, confirming the observations of

Hansen and Ginell (1989). The fabric's ability to elongate may be ultimately of less importance as a degraded textile artifact normally would not be subjected to stretching. In one case, the strength, extension at break, and energy to break of a crepe fabric were all drastically reduced after the addition of the parylene coating. The bonding action of parylene C was detrimental for this crepe fabric (fabric 5) because it likely reduced the ability of the fabric's high twist yarns to shift and straighten to accommodate the applied tensile force.

Fabric 8, an initially strong fabric displayed the highest statistically significant increase in tensile strength, and also stiffened the most. In contrast, fabric 6, a loosely constructed plain weave showed the least increase in tensile properties and also the least increase in flexural rigidity. Moisture regain declined slightly for all eight fabrics, from approximately 9.8% to 8.5% with the addition of the parylene C coating, a drop which appeared to only reflect only the change in mass due to the addition coating. The underlying silk appeared to have absorbed a similar amount of water vapour as the uncoated silk, indicating the coating was permeable to water vapour.

Effect of Light on Parylene Coated Silk Fabric

UV Filtered Light

After exposure to radiation with wave-lengths greater than 400 nm, the parylene C coated samples which had displayed a statistically significant increase in strength when first coated still remained stronger than their uncoated counterparts. Also, the weighted specimens showed a smaller drop in all three tensile properties if they were coated with parylene C; for example, the uncoated weighted specimens exhibited an 18% loss in extension at break, whereas the coated specimens lost only 5%. Even though the difference between the two was not statistically significant, it is possible visible light might be energetic enough to degrade the sensitive weighted silk, but not the parylene C coating. Because the coating would retain its consolidating qualities, the coated specimens would remain stronger than uncoated.

A noticeable change in colour occurred for both coated and uncoated fabrics, demonstrating light in the visible region of the spectrum had sufficient energy to cause prominent fading of the dyed fabrics, and bleaching of the undyed fabrics. Even though colour change was evident, the change in tensile strength, extension, energy to break, and flexibility for both coated and uncoated fabrics was not statistically significant. The exception was fabric 5, a weighted crepe fabric which showed a statistically significant drop in all three tensile properties after exposure to the full xenon arc spectrum.

The moisture regain of fabrics protected by the UV filter did not change if the specimens were coated, but the uncoated specimens for fabrics 3, 4 and 6 saw a statistically significant drop in this property. This loss in moisture regain is difficult to explain, especially as there was no apparent relationship between these changes in moisture regain, and the changes in other physical properties. Generally, a decline in a fibre's ability to absorb moisture could result from a loss of amorphous regions, or decreased accessibility to polar groups.

Simulated Daylight

All the properties tested underwent a measurably greater change when the fabrics were exposed to the full xenon arc spectrum which included both UV and visible light. Because the shorter wave-lengths of UV light have higher energy than visible light, they were more capable of initiating the chemical reactions which resulted in deterioration of tensile properties, increased rigidity and change in colour.

Upon full exposure to simulated daylight (250 kJ/m^2 at 420nm), the undyed silk specimens exhibited substantial yellowing when the parylene C coating was present. The yellowing of the corresponding uncoated specimens was barely perceptible. Despite their lack of colour change, these specimens and the yellowed coated specimens both showed a distinct loss in tensile strength, extension and energy to break. Of the four undyed fabrics, fabric 5, which was also weighted, displayed the largest loss in the tensile properties and also had the largest total colour change (ΔE) for the uncoated specimens. The dyed and weighted specimens (fabrics 1 to 4) faded drastically, this being accompanied by a large loss in tensile properties for both coated and uncoated specimens. Because of the large variation in readings within treatment groups, this loss could not be deemed statistically significant in some cases, even though the change in mean was considerable. After exposure to the full simulated daylight spectrum, there was no longer any statistically significant difference between the tensile properties of the coated and uncoated specimens in the majority of cases. This trend is in agreement with the results obtained by Hansen and Ginell (1989) in their study of parylene C-coated silk.

The deterioration in tensile properties of the uncoated fabrics was accompanied by an increase in rigidity. Weighted specimens showed the greatest deterioration in tensile properties and the largest increase in stiffness. As weighted silk is known to be highly sensitive to photodegradation, these results were not surprising. The tensile properties of the coated fabrics also deteriorated upon full exposure, but did not display a statistically significant or noticeable change in rigidity. Similarly, moisture regain showed a statistically significant decline for some uncoated specimens but not for any coated specimens.

Discolouration, loss in tensile strength and embrittlement are all consequences of photochemical oxidation (Schnabel & Kiwi, 1978). Both the silk protein (fibroin) and the parylene C polymer were likely altered by this type of degradation. The effects of photooxidation were more pronounced for samples exposed to the full spectrum than for UV-protected samples. In order for photochemical reactions to occur, light must be absorbed by the polymer. Because most polymers tend to absorb radiation with shorter, more energetic wave-lengths, UV radiation is responsible for most light-induced damage of polymeric materials. Once the energy from the light is absorbed, free radical chain reactions can be initiated by which oxygen-containing groups are introduced into the polymer chain resulting in measurable physical change (Schnabel, 1981). The uncoated specimens exhibited loss in tensile strength, extension, and energy to break as well as a slight colour change. According to Nakanishi and Kobayashi (cited in Lucas et al, 1958, p. 189; Robson, 1985, p.689) light-induced degradation of silk is thought to be due to the oxidation of tyrosine residues in combination with hydrolytic scission of the main chain polypeptide bonds. The undyed parylene C-coated fabrics yellowed more than their uncoated counterparts. SEM analysis showed the coating to have become embrittled, suggesting the coating itself is also undergoing degradation. IR spectra of UV exposed parylene C films show an increase in carbonyl content, demonstrating that oxidation has occurred (Nova Tran, internal report). The peak at 1695 cm^{-1} became more pronounced with increased exposure time, and is indicative of aromatic ketones which characteristically absorb between 1700 and 1689 cm^{-1}; therefore the carbonyl groups appear to be evolving from the methylene groups attached to the benzene ring structures. Studies on thermal oxidation of parylene C films also showed the formation of peaks in this region of the spectra (Nowlin et al., 1980).

According to the results from physical testing and SEM analysis, UV light is necessary to produce a statistically significant change in the properties of parylene C coated silk. Only when UV wave-lengths are present does there appear to be a problem with yellowing and embrittlement. For polymer degradation to manifest itself in a measurable change in a physical property, however, considerable damage must have already occurred. Chemical testing would be required to determine if any degradation occurred with exposure to visible light only.

Artificially vs Naturally Aged Fabrics

Fabric 8 was the one fabric used in this study which was artificially rather than naturally aged. Statistically significant differences were more easily discerned for this fabric because it was more uniform than the naturally aged fabrics. The artificially aged fabric was initially the strongest of the eight fabrics tested. It behaved in a similar manner to the other undyed, unweighted fabrics even though SEM revealed that the coating on fabric 8 was substantially different from the other specimens. The coated surface was irregular and globby, likely due to underlying surface debris which may have been deposited during the original artificial aging process. The irregularity of the coated surface may have been partially responsible for large initial increase in stiffness of fabric 8, which displayed the highest change in flexibility of all the fabrics. However, this increased stiffness may also have been a function of weave structure.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

Summary

Highly degraded silk artifacts are problematic for the textile conservator because there is no entirely satisfactory approach to treatment. The conformal polymer coating parylene C is one option to be considered when consolidation is required. Parylene C is transparent, colourless, flexible and strong. Its unique gas-phase deposition method allows extremely thin coatings (below 1 μm) to be applied which evenly coat all surfaces of the textile artifact down to the smallest fibril.

For parylene C to be used successfully as a conservation treatment, the coating must not only have a positive initial effect but must also resist degradation over time. The purpose of this research project was to study the initial effects of the parylene C coating on selected silk fabric properties, and how these properties change after photochemical aging through exposure to simulated daylight of varying wave-lengths. The fabric properties monitored were: total colour difference (ΔE), flexural rigidity, tensile strength, extension at break, energy to break, and moisture regain. Standard textile test methods were used in the determination of these properties. After completion of the physical testing, the data were analyzed using 3-way ANOVA and the Duncan's Multiple Range Test. In addition, scanning electron microscopy was employed to view the effects of the coating and light on the silk fibre surface.

Seven historic, or naturally aged silk fabrics were chosen for their variety in structure, strength, and presence of dye or weighting agents (Fabrics 1 to 7). In addition, one artificially light-aged sample was studied (Fabric 8). The fabrics were coated with approximately 0.8 μm of parylene C at the Nova Tran laboratory in Clear Lake WI, using a Parylene Deposition System model 1050.

Fabric structure was important in determining the initial effect of the coating on fabric properties. Fabrics with a smooth surface combined with a dark colour (Fabrics 2, 3, and 4) had an iridescent appearance upon application of parylene C due to the formation of interference bands, a phenomenon which only occurs when very thin coatings are used. Fabrics with compact weaves (fabrics 3, 4, and 8 especially) also became noticeably more rigid than those with more open constructions (fabrics 2, 6, and 7). Stiffness was increased because the coating reduced the yarns' ability to move: SEM analysis showed fibres in close proximity to one another could become bonded to each other by the coating, and that tiny fibrils which had detached from some fibres were bonded across neighbouring fibres. Application of the parylene C coating was detrimental to the tensile properties of a crepe fabric tested (fabric 5) because the coating prevented the very high twist yarns used in its construction from being able to shift to accommodate the applied tensile force.

The spot welding of fibres is one way in which the parylene C polymer imparts greater strength to degraded materials. Statistically significant increases in strength were only noted for fabrics 7 and 8 which had low standard deviations and were initially stable before coating. Even though statistical significance could not be established for the initially weaker fabrics, they were nonetheless more easily handled after the coating was applied. The initial effect of the coating on tensile properties was difficult to evaluate for fabrics 1 to 4 due to the high variability of these naturally aged silk samples.

Parylene C coatings are known to be impermeable to liquid water, and have a low water vapour permeability (Nova Tran, 1990). Results from the present study showed coated fabrics likely absorbed a similar amount of water vapour as uncoated. The lower moisture regain of the coated fabrics could largely be accounted for by the increased mass of the coated specimens.

Stability to light is important because all museum artifacts are exposed to light during examination or display. In order to evaluate the long-term effect of light on parylene C-coated silk fabrics, measurements of the fabrics' physical properties were taken after accelerated photochemical aging, and compared to the properties of the unexposed control samples. For this study, accelerated light aging was performed in a xenon-arc Weather-Ometer using AATCC test method 16E-1987 as a guide. Samples were exposed to 250 kJ/m^2 with a lamp irradiance of 0.75 w/m^2 measured at 420 nm; the relative humidity was 65 ± 5% and the black panel temperature was 50 ± 2 °C. The coated and uncoated specimens were randomly assigned to four light treatment groups, two of which were control groups. Control group A was not placed in the Weather-Ometer, while control group B endured the relative humidity and temperature conditions within the aging chamber, but was masked from light exposure. Two treatment groups were exposed to different light-exposure conditions: group C was protected from xenon-arc radiation with wave-lengths below 400 nm by a UV filter, while specimens in group D were exposed to the full simulated daylight spectrum emitted by the xenon arc lamp.

The specimens in group C, which were protected by the UV filter, showed a visible change in colour; dyed fabrics faded while undyed fabrics bleached. Despite the change in colour, however, seven of the eight fabrics showed no statistically significant decline in tensile properties. In general, the weighted specimens (fabrics 1 to 5) showed a greater loss in physical properties than did the unweighted. Flexibility was not affected significantly when radiation with wave-lengths below 400 nm was excluded.

Those coated fabrics which exhibited a statistically significant increase in tensile strength before light exposure (fabrics 7 and 8) remained stronger as long as they were protected by the UV filtering film. When the specimens in group D were exposed to the full xenon arc spectrum, however, a noticeable change occurred in all the properties measured. The coated samples lost sufficient strength for there no longer to be a statistically significant difference between the coated and uncoated samples. Both coated and uncoated dyed samples faded drastically, and a yellowing of the coating was apparent on the fully exposed undyed specimens in group D. The flexibility of the uncoated fabrics in this group decreased measurably but the coated samples did not change. Similarly, some uncoated samples showed a decrease in moisture regain while the moisture regain of the coated samples remained virtually constant. SEM analysis revealed the parylene C coating had become embrittled and cracked under stress after it had been exposed to the full xenon arc spectrum. Researchers have shown both silk (Harris, 1934) and parylene (Beach et al., 1990) are susceptible to photochemical oxidation, which is known to cause yellowing, embrittlement, and decreased tensile strength.

From this research several conclusions were drawn. The parylene C coating was capable of providing some consolidation for weak fabrics even at coatings less than 1 μm thick. The accompanying changes in flexibility and possibly appearance may not be of primary importance when consolidation of an artifact in a highly degraded state is vital for it to remain intact. The coating retained its beneficial properties when exposed to visible light but degraded when higher energy UV light was present.

Conclusions

In order for parylene C to be used successfully as a conservation treatment, the coating must not only be beneficial initially, but must also be stable to light. This research showed that a coating less than one micron thick on naturally aged, degraded silk fabric made highly deteriorated fabrics easier to handle, even though statistically significant differences in tensile properties could not be established in some cases. This thin coating also caused a noticeable stiffening of all fabrics tested. Fabrics could still bend under their own weight, but the drapability was reduced because the yarns were no longer as free to shift within the fabric structure.

The parylene-C coating retained its beneficial consolidating properties with exposure to visible light, but was not capable of slowing down the degradation of silk if wave-lengths below 400 nm were present. With exposure to UV light, the thin coating yellowed noticeably, and became embrittled as revealed by SEM. It is therefore of paramount importance that artifacts consolidated with parylene C be protected from harmful ultraviolet radiation. This treatment is not well suited for artifacts which would be exposed to direct sunlight, as might occur at an historic site. Also, care must be taken that light sources used for the exhibition or the examination of parylene C-coated textiles are free of UV radiation.

Because the impact of the parylene C coating was found to depend on several factors including fabric construction, colour of dye, and the initial strength of the fabric, a general method for parylene's use on all textiles cannot be recommended. Each must be evaluated on an individual basis to determine if the coating is a suitable treatment option. Because parylene is an irreversible technique, the decision to coat a textile artifact with this polymer must be carefully made; however, for highly degraded silk artifacts for which there is no other viable option, this treatment may be appropriate. Embrittled weighted silks often cannot be sewn to a support backing because piercing the fabric with a needle and thread may cause fragile yarns to break away to form holes. Also, the stitches may exert enough pressure to break the weak textile yarns. Parylene is unique in that it provides a protective sheath for each fibre in a fabric; it does not merely consolidate the surface. In addition, the gas-phase deposition process for parylene produces a thinner and more highly conformal coating than can be achieved by liquid-based consolidants or adhesives.

Recommendations for Future Research

As most museum objects are not exposed to the full daylight spectrum, expanded research is in order to investigate more fully the effect of visible light only, or other lighting conditions found commonly in the museum environment. Tests which detect chemical changes could be used to determine if any degradation occurs when UV light is excluded. It may also be useful to compare the effectiveness parylene coating C with more conventional consolidation techniques, like stitching, or other polymers.

Artificially aged silk fabrics should be considered for use in further research in this area because the artificially aged specimens were more uniform than naturally aged; their lower standard deviation allowed statistically significant differences between treatment groups to be more readily determined.

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APPENDIX A-1: Additional Procedures

WASHING PROCEDURE

Each of the eight fabrics chosen for study was washed separately using the following procedure. After the naturally aged fabrics (fabrics 1 to 7) had been cut into panels, the panels were sewn between two layers of netting to provide support. The panels were then immersed in a tray of distilled water (approximately 37 °C) and allowed to soak for 10 minutes, and agitated slightly. The fabric was then washed for 10 to 15 minutes in a 0.2% solution of Shurgain anionic surfactant in distilled water, at a temperature of about 37 °C. A small sponge was used to provide gentle agitation. The fabric was then rinsed 4 times in distilled or tap water, with the temperature decreasing with each rinse. While still in the net, the fabric panels were blotted with cotton toweling to remove excess moisture. They were then removed from the netting and allowed to dry on a flat, smooth surface. The fabric was not pinned down while drying, but wrinkles and creases were gently smoothed out while the fabric was wet.

The new fabric which was to undergo artificial aging (fabric 8) was washed in three sections (approximately 1 x 1 m each) before being cut into 14 x 7 cm specimens. The procedure described above was followed, only the fabric did not require sandwiching between layers of netting, as it was strong and stable.

ARTIFICIAL AGING PROCEDURE

One of the eight fabrics studied for this project (fabric 8) was artificially light-aged prior to the application of the parylene C polymer coating. The new degummed undyed twill fabric from TestFabrics Inc.[4] was first washed and then cut into warp specimens measuring 14 x 7cm (LxW).

The specimens were then artificially aged using a procedure based on AATCC test method 16E-1987 "Colorfastness to Light: Water-Cooled Xenon-Arc Lamp, Continuous Light". An Atlas Weather-Ometer model Ci35W outfitted with a xenon arc lamp filtered to simulate the daylight spectrum with borosilicate filters was used. The specimens were inserted into standard test specimen holders and backed with acid-free mat board. The holders were then clipped inside the Weather-Ometer aging chamber and were irradiated with 300 kJ of energy, which took approximately 110 hours. The lamp had an irradiance of 0.75 w/m^2 measured at 420 nm, the relative humidity was 65 ± 5% and the black panel temperature was set for 50 ± 2 °C, the same conditions employed by Hansen and Ginell (1989). Upon completion of the aging process, the specimens were removed from the holders and stored in darkness until the parylene C coating was applied.

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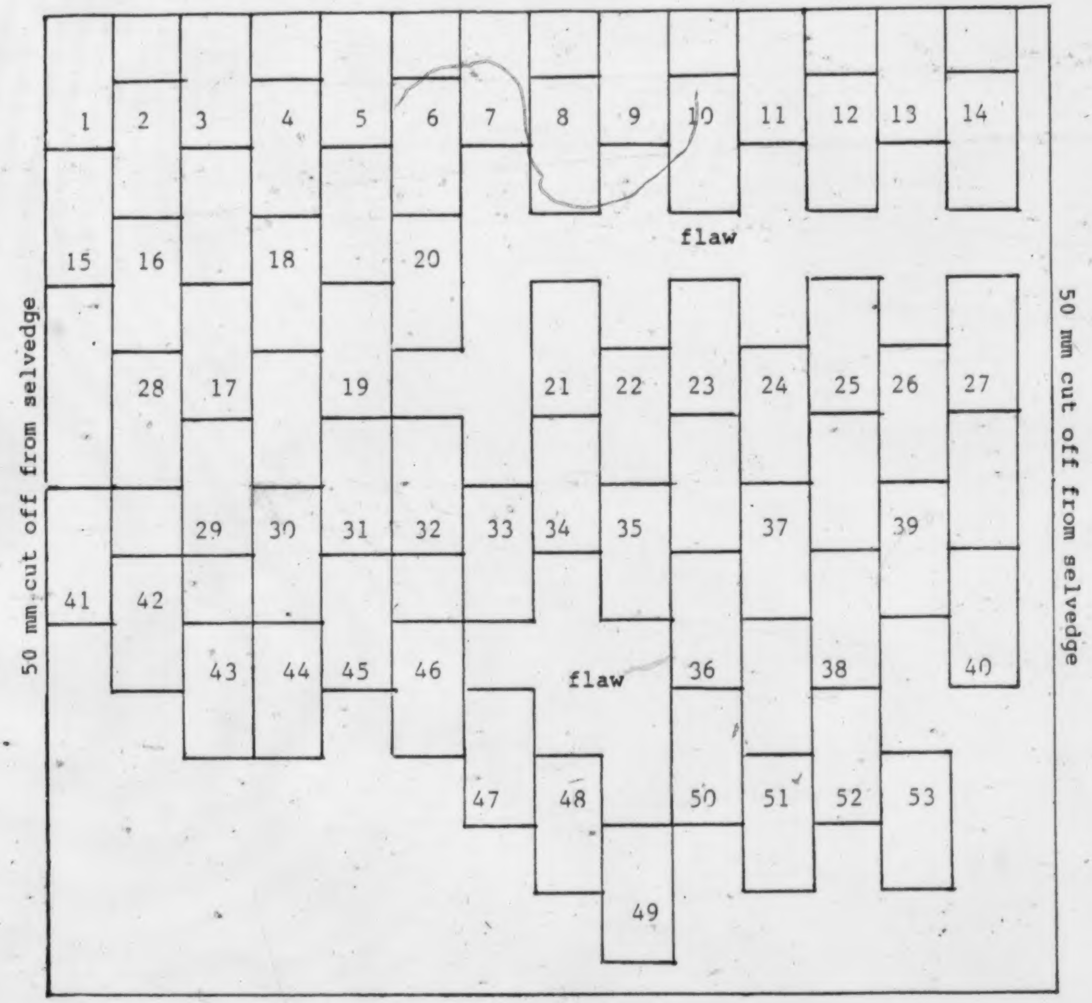
[4] TestFabrics Inc. P.O. Drawer 0 200 Blackford Ave. Middlesex NJ 08846

APPENDIX A-2: Cutting Diagram for Artificially Aged Specimens

Cutting Diagram: Fabric 8 (TestFabrics #609)
Samples for artificial aging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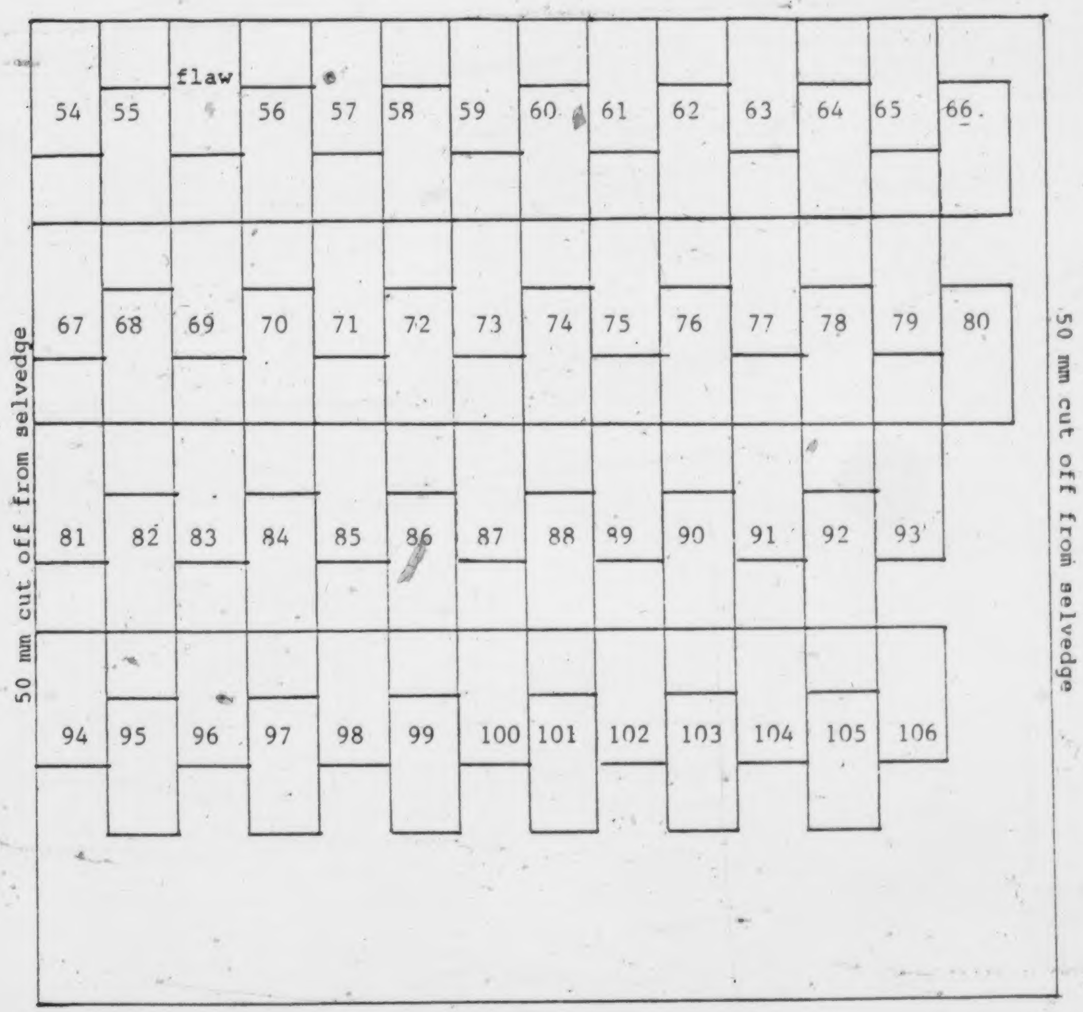
3
4
5
6
7
8
9
10
11
12
13
14
flaw
15
16
18
20
50 mm cut off from selvedge
28
17
19
21
22
23
24
25
26
27
50 mm cut off from selvedge
29
30
31
32
33
34
35
37
39
41
42
43
44
45
46
flaw
36
38
40
47
48
50
51
52
53
49

Scale: 1:7

Cutting Diagram (cont.): Fabric 8 (TestFabrics #609)
Samples for artificial aging


flaw
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106
50 mm cut off from selvedge
50 mm cut off from selvedge

Scale: 1:7

APPENDIX A-3: Summary of Raw Data

Colour Change (CIElab* values)

Fabric # and treatment	L* mean	L* SD	a* mean	a* SD	b* mean	b* SD
Fabric 1						
uncoated						
unexposed	45.0	0.32	9.4	0.17	2.5	0.13
masked	45.4	0.41	9.3	1.0	2.0	0.45
UV-filter	54.4	0.49	3.1	0.05	2.3	0.19
full	63.1	0.02	1.7	0.24	9.9	0.21
coated						
unexposed	45.4	0.16	9.2	1.0	2.0	0.45
masked	45.3	0.26	8.4	0.28	2.3	0.30
UV-filter	52.8	0.12	3.1	0.07	2.4	0.21
full	57.2	0.56	2.8	0.42	10.0	0.43
Fabric 2						
uncoated						
unexposed	19.5	0.48	0.67	0.32	-0.11	0.33
masked	19.5	0.34	0.75	0.16	0.12	0.12
UV-filter	24.4	0.37	-0.70	0.06	2.4	0.36
full	28.3	0.42	5.0	0.32	4.5	0.57
coated						
unexposed	21.5	0.18	1.8	1.3	-1.2	0.5
masked	22.1	0.49	0.27	1.8	-0.04	1.26
UV-filter	26.6	0.27	-0.6	1.9	1.9	1.0
full	26.4	0.4	4.1	1.4	1.6	0.95
Fabric 3						
uncoated						
unexposed	38.4	0.35	19.2	0.19	15.1	0.18
masked	38.3	0.18	19.6	0.28	15.3	0.27
UV-filter	41.3	0.58	12.4	0.32	16.8	0.17
full	54.3	0.46	5.5	0.05	-3.0	0.17
coated						
unexposed	38.0	0.61	17.1	1.2	13.7	0.61
masked	39.1	0.35	18.0	0.75	13.8	0.28
UV-filter	41.1	0.22	11.0	0.66	15.9	0.41
full	46.8	1.4	7.6	0.48	-5.0	0.50

Fabric # and treatment	L*		a*		b*	
	mean	SD	mean	SD	mean	SD
Fabric 4						
uncoated						
unexposed	22.8	0.25	27.9	0.2	-1.3	0.16
masked	23.0	0.31	22.0	0.23	-1.3	0.09
UV-filter	25.8	0.33	19.2	.19	-2.7	0.09
full	32.0	0.32	20.0	0.40	-2.5	0.36
coated						
unexposed	24.7	0.20	17.4	1.3	-2.1	0.61
masked	24.7	0.21	19.2	0.82	-2.7	0.45
UV-filter	26.8	0.25	16.3	1.7	-3.4	0.68
full	28.9	0.29	18.8	0.65	-2.9	0.30
Fabric 5						
uncoated						
unexposed	82.0	0.60	0.04	0.12	12.8	0.26
masked	82.4	0.35	0.19	0.09	13.0	0.20
UV-filter	84.8	0.21	0.27	0.02	9.4	0.26
full	82.5	0.64	-0.57	0.05	16.2	0.58
coated						
unexposed	81.4	0.22	-0.18	0.09	12.6	0.17
masked	81.5	0.08	0.14	0.13	12.3	0.21
UV-filter	83.5	0.26	0.08	0.08	9.4	0.28
full	78.9	0.42	-1.1	0.09	22.2	0.46
Fabric 6						
uncoated						
unexposed	67.2	0.18	-0.11	0.03	10.5	0.12
masked	67.8	0.18	-0.19	0.04	10.1	0.07
UV-filter	68.6	0.15	0.26	0.04	7.3	0.13
full	69.0	0.14	-0.06	0.03	8.7	0.07
coated						
unexposed	66.8	0.11	-0.15	0.04	10.0	0.04
masked	66.3	0.21	-0.12	0.04	9.6	0.11
UV-filter	66.4	0.59	0.31	0.12	1.8	0.10
full	64.8	0.13	-1.2	0.03	17.7	0.26

Fabric # and treatment	L* mean	L* SD	a* mean	a* SD	b* mean	b* SD
Fabric 7						
uncoated						
unexposed	85.4	0.36	-0.30	0.03	8.3	0.30
masked	85.2	0.22	-0.30	.03	8.3	0.19
UV-filter	86.2	0.34	0.13	0.07	5.1	0.11
full	84.3	0.21	0.21	0.04	8.8	0.10
coated						
unexposed	84.2	0.32	-0.50	0.26	8.0	0.39
masked	83.9	0.35	-0.50	0.17	8.2	0.29
UV-filter	84.6	0.36	-0.18	0.17	5.1	0.21
full	81.0	0.17	0.70	0.19	21.4	0.71
Fabric 8						
uncoated						
unexposed	90.6	0.12	-0.05	0.11	8.34	0.24
masked	90.5	0.08	-0.33	0.01	9.6	0.11
UV-filter	90.9	0.19	0.02	0.02	6.9	0.17
full	90.0	0.08	-0.11	0.03	8.8	0.10
coated						
unexposed	89.9	0.09	-0.25	0.07	9.8	0.17
masked	90.1	0.13	-0.39	0.07	10.0	0.16
UV-filter	90.5	0.09	-0.12	0.05	7.2	0.12
full	87.8	0.05	-0.79	0.08	24.8	0.46

Note. n=6 for all fabrics, except fabrics 1 and 5 where n=3. Four readings averaged for each specimen.

```
fabric # and treatment                            Mean    Std Dev    Cases

For Entire Population                           3.8592     5.3215      336

FAB                 1                           7.4250     7.9036       24
  COAT              1  no                       8.2250     9.0728       12
    EXP             1  control                   .0000      .0000        3
    EXP             2  masked                    .5333      .3786        3
    EXP             3  uv filter               11.3000      .4359        3
    EXP             4  full exposure           21.0667      .8021        3

  COAT              2  yes                      6.6250     6.8482       12
    EXP             1  control                   .0000      .0000        3
    EXP             2  masked                    .9667      .1155        3
    EXP             3  uv filter                9.5667      .1528        3
    EXP             4  full exposure           15.9667      .4041        3

FAB                 2                           3.9812     3.7486       48
  COAT              1  no                       4.1500     4.4717       24
    EXP             1  control                   .0000      .0000        6
    EXP             2  masked                    .3833      .1169        6
    EXP             3  uv filter                5.5000      .4775        6
    EXP             4  full exposure           10.7167      .3430        6

  COAT              2  yes                      3.8125     2.9425       24
    EXP             1  control                   .0000      .0000        6
    EXP             2  masked                   2.6167     1.9031        6
    EXP             3  uv filter                5.7667     1.0948        6
    EXP             4  full exposure            6.8667      .2733        6

FAB                 3                           7.0958     8.3373       48
  COAT              1  no                       8.1458     9.9885       24
    EXP             1  control                   .0000      .0000        6
    EXP             2  masked                    .6833      .2927        6
    EXP             3  uv filter                7.6333      .3386        6
    EXP             4  full exposure           24.2667      .3445        6

  COAT              2  yes                      6.0458     6.3223       24
    EXP             1  control                   .0000      .0000        6
    EXP             2  masked                   1.4167      .4875        6
    EXP             3  uv filter                7.0833      .7360        6
    EXP             4  full exposure           15.6833      .8727        6

FAB                 4                           2.9958     3.0629       48
  COAT              1  no                       3.5333     3.9314       24
    EXP             1  control                   .0000      .0000        6
    EXP             2  masked                    .3167      .0983        6
    EXP             3  uv filter                4.3167      .3371        6
    EXP             4  full exposure            9.5000      .3464        6

  COAT              2  yes                      2.4583     1.7639       24
    EXP             1  control                   .0000      .0000        6
    EXP             2  masked                   2.1167      .9283        6
    EXP             3  uv filter                3.1500      .2429        6
    EXP             4  full exposure            4.5667      .3011        6

FAB                 5                           2.8792     3.2911       24
  COAT              1  no                       2.1417     2.0111       12
    EXP             1  control                   .0000      .0000        3
    EXP             2  masked                    .5333      .1528        3
    EXP             3  uv filter                4.3667      .3512        3
    EXP             4  full exposure            3.6667      .6506        3

  COAT              2  yes                      3.6167     4.1733       12
    EXP             1  control                   .0000      .0000        3
    EXP             2  masked                    .5667      .2309        3
    EXP             3  uv filter                3.8667      .3786        3
    EXP             4  full exposure           10.0333      .4041        3
```

Colour Change (ΔE) (cont.)

```
fabric # and treatment                          Mean    Std Dev    Cases

FAB                   6                        2.2917    2.5238      48
  COAT                1  no                    1.6458    1.3941      24
    EXP               1  control                .0000     .0000       6
    EXP               2  masked                 .6833     .1169       6
    EXP               3  uv filter             3.3833     .4602       6
    EXP               4  full exposure         2.5167     .0753       6

  COAT                2  yes                   2.9375    3.1941      24
    EXP               1  control                .0000     .0000       6
    EXP               2  masked                 .5333     .1211       6
    EXP               3  uv filter             3.3333     .0516       6
    EXP               4  full exposure         7.8833     .2858       6

FAB                   7                        2.7750    4.3822      48
  COAT                1  no                    1.2208    1.3322      24
    EXP               1  control                .0000     .0000       6
    EXP               2  masked                 .3500     .1871       6
    EXP               3  uv filter             3.3333     .1633       6
    EXP               4  full exposure         1.2000     .2191       6

  COAT                2  yes                   4.3292    5.6944      24
    EXP               1  control                .0000     .0000       6
    EXP               2  masked                 .5000     .2608       6
    EXP               3  uv filter             3.0667     .2875       6
    EXP               4  full exposure        13.7500     .7148       6

FAB                   8                        2.7229    4.8963      48
  COAT                1  no                     .8542     .6554      24
    EXP               1  control                .0000     .0000       6
    EXP               2  masked                1.0167     .1169       6
    EXP               3  uv filter             1.7500     .1871       6
    EXP               4  full exposure          .6500     .0837       6

  COAT                2  yes                   4.5917    6.4244      24
    EXP               1  control                .0000     .0000       6
    EXP               2  masked                 .3667     .0516       6
    EXP               3  uv filter             2.6667     .1633       6
    EXP               4  full exposure        15.3333     .4457       6

  Total Cases = 336
```

```
fabric # and treatment                                 Mean     Std Dev    Cases

For Entire Population                                18.8116     8.1685      146

FAB                  5                               22.1762     6.6274       21
  COAT               1  no                           20.9556     4.7852        9
    EXP              2  masked                       21.2000      .3606        3
    EXP              3  uv filter                    15.3667      .4509        3
    EXP              4  full exposure                26.3000     1.2124        3

  COAT               2  yes                          23.0917     7.8148       12
    EXP              1  control                      20.8667      .3055        3
    EXP              2  masked                       20.2333      .4041        3
    EXP              3  uv filter                    15.7000      .4359        3
    EXP              4  full exposure                35.5667      .6110        3

FAB                  6                               19.4195     6.2370       41
  COAT               1  no                           16.8444     2.1569       18
    EXP              2  masked                       19.4667      .0816        6
    EXP              3  uv filter                    14.3500      .2429        6
    EXP              4  full exposure                16.7167      .1169        6

  COAT               2  yes                          21.4348     7.5803       23
    EXP              1  control                      19.5667      .0516        6
    EXP              2  masked                       19.0400      .1817        5
    EXP              3  uv filter                    13.5000      .1265        6
    EXP              4  full exposure                33.2333      .5125        6

FAB                  7                               18.5190     9.8922       42
  COAT               1  no                           15.1389     3.2596       18
    EXP              2  masked                       16.8333      .4033        6
    EXP              3  uv filter                    10.7167      .2563        6
    EXP              4  full exposure                17.8667      .2338        6

  COAT               2  yes                          21.0542    12.2857       24
    EXP              1  control                      16.1833      .6911        6
    EXP              2  masked                       16.2500      .6221        6
    EXP              3  uv filter                    10.3500      .4278        6
    EXP              4  full exposure                41.4333     1.1112        6

FAB                  8                               16.8286     8.2742       42
  COAT               1  no                           13.1444     1.8222       18
    EXP              2  masked                       14.8833      .1722        6
    EXP              3  uv filter                    10.7500      .4593        6
    EXP              4  full exposure                13.8000      .1549        6

  COAT               2  yes                          19.5917    10.0498       24
    EXP              1  control                      15.2167      .2787        6
    EXP              2  masked                       15.4500      .2588        6
    EXP              3  uv filter                    11.3167      .2137        6
    EXP              4  full exposure                36.3833      .5742        6

  Total Cases = 336
```

Flexural Rigidity (mg-cm)

```
fabric # and treatment                           Mean     Std Dev    Cases

For Entire Population                          62.4496    62.6637     574

FAB            1                               33.2301    18.9799      48
  COAT         1   no                          15.2398     5.7051      24
    EXP        1   control                     10.3268     1.5298       6
    EXP        2   masked                      13.0595     1.8283       6
    EXP        3   uv filter                   13.4929     1.5788       6
    EXP        4   full exposure               24.0798     3.0726       6

  COAT         2   yes                         51.2203     5.3052      24
    EXP        1   control                     48.3262     5.0893       6
    EXP        2   masked                      49.8482     2.6966       6
    EXP        3   uv filter                   49.9217     4.6573       6
    EXP        4   full exposure               56.7854     4.8071       6

FAB            2                               34.9845    18.3724      80
  COAT         1   no                          20.4972     7.5632      40
    EXP        1   control                     13.4090     3.6180      10
    EXP        2   masked                      18.8267     6.5911      10
    EXP        3   uv filter                   21.2935     5.3223      10
    EXP        4   full exposure               28.4597     5.7395      10

  COAT         2   yes                         49.4717    14.0008      40
    EXP        1   control                     42.9363    19.2107      10
    EXP        2   masked                      57.8427    14.7422      10
    EXP        3   uv filter                   50.4221     4.8477      10
    EXP        4   full exposure               46.6856    10.2275      10

FAB            3                               54.5211    35.4904      80
  COAT         1   no                          20.1722     8.1331      40
    EXP        1   control                     14.8366     1.7202      10
    EXP        2   masked                      15.8750     2.3196      10
    EXP        3   uv filter                   16.3210     1.3552      10
    EXP        4   full exposure               33.6560     2.4125      10

  COAT         2   yes                         88.8700     8.0673      40
    EXP        1   control                     83.1401     6.1506      10
    EXP        2   masked                      94.4482     8.4633      10
    EXP        3   uv filter                   88.7103     8.0121      10
    EXP        4   full exposure               89.1815     6.0976      10

FAB            4                              110.9288    75.7342      79
  COAT         1   no                          36.6243    13.6725      39
    EXP        1   control                     29.7449     1.9916      10
    EXP        2   masked                      28.5072     2.3328       9
    EXP        3   uv filter                   28.6559     2.3840      10
    EXP        4   full exposure               58.7774     6.3636      10

  COAT         2   yes                        183.3756    19.6194      40
    EXP        1   control                    185.7504    28.8933      10
    EXP        2   masked                     173.1347    13.0380      10
    EXP        3   uv filter                  193.1189    17.2519      10
    EXP        4   full exposure              181.4985    11.5483      10

FAB            5                               38.7729    21.7585      48
  COAT         1   no                          20.1816    12.9463      24
    EXP        1   control                     12.6743      .7755       6
    EXP        2   masked                      13.0961     1.0074       6
    EXP        3   uv filter                   13.3733     2.0240       6
    EXP        4   full exposure               41.5828     5.6711       6

  COAT         2   yes                         57.3643     8.8607      24
    EXP        1   control                     55.3160     6.2229       6
    EXP        2   masked                      52.2979     4.9234       6
    EXP        3   uv filter                   53.5364     6.2303       6
    EXP        4   full exposure               68.3068     7.8912       6
```

Flexural Rigidity (mg-cm) (cont.)

```
 fabric # and treatment                              Mean      Std Dev    Cases

FAB                  6                             25.4262     7.2286        80
  COAT               1   no                        18.7770     3.3919        40
    EXP              1   control                   16.5799     2.6327        10
    EXP              2   masked                    17.3003     1.8003        10
    EXP              3   uv filter                 18.6806     3.8455        10
    EXP              4   full exposure             22.5471     1.1429        10

  COAT               2   yes                       32.0754     1.9103        40
    EXP              1   control                   31.9761     1.2784        10
    EXP              2   masked                    31.9917     1.8536        10
    EXP              3   uv filter                 32.0274     2.6916        10
    EXP              4   full exposure             32.3064     1.8487        10

FAB                  7                             49.1369    21.9174        79
  COAT               1   no                        30.3099     9.5140        40
    EXP              1   control                   24.2077     3.6430        10
    EXP              2   masked                    27.7474     6.2279        10
    EXP              3   uv filter                 28.5770     9.7945        10
    EXP              4   full exposure             40.7075     8.4922        10

  COAT               2   yes                       68.4467    11.7191        39
    EXP              1   control                   64.6819     5.2658        10
    EXP              2   masked                    62.0850     8.4814        10
    EXP              3   uv filter                 73.5588    12.0869         9
    EXP              4   full exposure             73.9722    15.1516        10

FAB                  8                            131.8777    98.5640        80
  COAT               1   no                        35.4714    10.1729        40
    EXP              1   control                   34.1307     7.9193        10
    EXP              2   masked                    29.8365     8.1971        10
    EXP              3   uv filter                 30.1586     5.0112        10
    EXP              4   full exposure             47.7597     7.5503        10

  COAT               2   yes                      228.2840    22.5911        40
    EXP              1   control                  233.7421    15.8916        10
    EXP              2   masked                   236.7000    27.9494        10
    EXP              3   uv filter                213.1403    18.4923        10
    EXP              4   full exposure            229.5536    21.6211        10

  Total Cases = 672
```

Tensile Strength (N)

```
fabric # and treatment
                                                   Mean     Std Dev     Cases

For Entire Population                            34.5125    29.2816      560

FAB                  1                            4.7200     2.9771       40
  COAT               1  no                        3.9404     2.9063       20
    EXP              1  control                   4.1202     1.8512        5
    EXP              2  masked                    6.9043     3.4823        5
    EXP              3  uv filter                 2.7176     2.3269        5
    EXP              4  full exposure             2.0197     1.2852        5

  COAT               2  yes                       5.4995     2.9098       20
    EXP              1  control                   5.5152     1.5767        5
    EXP              2  masked                    4.9246     2.9167        5
    EXP              3  uv filter                 8.1855     3.5401        5
    EXP              4  full exposure             3.3727     1.2681        5

FAB                  2                           37.1139    19.2790       80
  COAT               1  no                       35.1375    19.5489       40
    EXP              1  control                  42.5852     7.4641       10
    EXP              2  masked                   45.5773     9.9293       10
    EXP              3  uv filter                48.5104     5.8238       10
    EXP              4  full exposure             3.8769      .7459       10

  COAT               2  yes                      39.0904    19.0452       40
    EXP              1  control                  46.5975    11.5902       10
    EXP              2  masked                   53.5920     5.5394       10
    EXP              3  uv filter                47.4313     2.7191       10
    EXP              4  full exposure             8.7407     1.5305       10

FAB                  3                           11.2296     7.4446       80
  COAT               1  no                        7.5206     5.8749       40
    EXP              1  control                   9.4961     6.6612       10
    EXP              2  masked                   10.3800     6.5440       10
    EXP              3  uv filter                 7.6214     4.5674       10
    EXP              4  full exposure             2.5848     1.0016       10

  COAT               2  yes                      14.9387     7.0378       40
    EXP              1  control                  18.3202     5.4033       10
    EXP              2  masked                   19.9241     3.9772       10
    EXP              3  uv filter                16.0423     5.2400       10
    EXP              4  full exposure             5.4681      .9120       10

FAB                  4                           10.2506     5.4248       79
  COAT               1  no                       10.1000     4.4248       39
    EXP              1  control                  12.4665     3.9184       10
    EXP              2  masked                   11.4352     4.4039        9
    EXP              3  uv filter                10.2809     3.8439       10
    EXP              4  full exposure             6.3510     3.4117       10

  COAT               2  yes                      10.3974     6.3035       40
    EXP              1  control                  14.4109     5.4214       10
    EXP              2  masked                    8.9330     3.9912       10
    EXP              3  uv filter                13.7870     5.9664       10
    EXP              4  full exposure             4.4586     4.3622       10

FAB                  5                           31.1078    23.2066       40
  COAT               1  no                       40.2808    26.8741       20
    EXP              1  control                  65.2954     4.3820        5
    EXP              2  masked                   43.4975    24.8849        5
    EXP              3  uv filter                46.8329    20.5269        5
    EXP              4  full exposure             5.4975     3.1021        5

  COAT               2  yes                      21.9348    14.3553       20
    EXP              1  control                  25.3883     2.1159        5
    EXP              2  masked                   24.3484     3.7403        5
    EXP              3  uv filter                31.8629    21.8264        5
    EXP              4  full exposure             6.1397     5.1715        5
```

Tensile Strength (N) (cont.)

```
 fabric # and treatment                            Mean      Std Dev    Cases

FAB                   6                          19.8824     2.7090      80
  COAT                1  no                      18.9922     2.5772      40
    EXP               1  control                 20.3459      .7986      10
    EXP               2  masked                  20.7285     1.0617      10
    EXP               3  uv filter               19.9535     1.4225      10
    EXP               4  full exposure           14.9406      .5850      10

  COAT                2  yes                     20.7727     2.5685      40
    EXP               1  control                 21.3466     2.3035      10
    EXP               2  masked                  22.7592     1.4171      10
    EXP               3  uv filter               21.3564     2.0733      10
    EXP               4  full exposure           17.6286      .9284      10

FAB                   7                          64.8235    12.6264      81
  COAT                1  no                      60.5277     9.9756      41
    EXP               1  control                 64.0201     5.0708      10
    EXP               2  masked                  63.4380     6.7045      12
    EXP               3  uv filter               66.2175     8.5098      10
    EXP               4  full exposure           46.4449     5.8159       9

  COAT                2  yes                     69.2267    13.6264      40
    EXP               1  control                 74.1047     8.9844      10
    EXP               2  masked                  77.5971     7.8893      10
    EXP               3  uv filter               73.2316    10.5250      10
    EXP               4  full exposure           51.9734     9.9000      10

FAB                   8                          79.6915    18.6100      80
  COAT                1  no                      73.0919    11.7570      40
    EXP               1  control                 80.2164     3.5603      10
    EXP               2  masked                  77.4107     3.6579      10
    EXP               3  uv filter               79.8043     5.4308      10
    EXP               4  full exposure           54.9360     7.0702      10

  COAT                2  yes                     86.2912    21.7708      40
    EXP               1  control                 99.4636     6.8434      10
    EXP               2  masked                  99.5126     6.5361      10
    EXP               3  uv filter               95.3728     8.3330      10
    EXP               4  full exposure           50.8158     4.2283      10

  Total Cases = 672
```

Extension to Break (%)

```
fabric # and treatment                              Mean    Std Dev    Cases

For Entire Population                             6.5067     4.0031      559

FAB                     1                         1.6844      .6113       39
  COAT                  1  no                     2.0187      .5971       20
    EXP                 1  control                2.1733      .4337        5
    EXP                 2  masked                 2.4507      .4287        5
    EXP                 3  uv filter              2.0293      .7520        5
    EXP                 4  full exposure          1.4213      .2166        5

  COAT                  2  yes                    1.3326      .3972       19
    EXP                 1  control                1.4080      .3509        5
    EXP                 2  masked                 1.3093      .3896        5
    EXP                 3  uv filter              1.6160      .3845        5
    EXP                 4  full exposure           .9133      .0658        4

FAB                     2                         8.0420     3.3560       80
  COAT                  1  no                     7.8740     3.2553       40
    EXP                 1  control               10.4960      .9148       10
    EXP                 2  masked                 9.4107      .9014       10
    EXP                 3  uv filter              9.0013     1.2010       10
    EXP                 4  full exposure          2.5880      .3296       10

  COAT                  2  yes                    8.2100     3.4870       40
    EXP                 1  control               11.0760     1.2361       10
    EXP                 2  masked                10.0653     1.8165       10
    EXP                 3  uv filter              8.9587      .9754       10
    EXP                 4  full exposure          2.7400      .3013       10

FAB                     3                         2.5467     1.0245       80
  COAT                  1  no                     2.5097     1.0276       40
    EXP                 1  control                3.2173      .9246       10
    EXP                 2  masked                 3.1573      .4110       10
    EXP                 3  uv filter              2.5773      .4769       10
    EXP                 4  full exposure          1.0867      .2162       10

  COAT                  2  yes                    2.5837     1.0332       40
    EXP                 1  control                3.3040      .9050       10
    EXP                 2  masked                 3.0547      .6767       10
    EXP                 3  uv filter              2.7213      .7048       10
    EXP                 4  full exposure          1.2547      .2124       10

FAB                     4                         1.7765      .8232       79
  COAT                  1  no                     2.3371      .6939       39
    EXP                 1  control                2.9640      .5283       10
    EXP                 2  masked                 2.6163      .4356        9
    EXP                 3  uv filter              2.3173      .3694       10
    EXP                 4  full exposure          1.4787      .3387       10

  COAT                  2  yes                    1.2300      .5155       40
    EXP                 1  control                1.4827      .5350       10
    EXP                 2  masked                 1.2267      .3152       10
    EXP                 3  uv filter              1.5187      .3460       10
    EXP                 4  full exposure           .6920      .4013       10

FAB                     5                         6.5257     3.2275       40
  COAT                  1  no                     8.0580     3.5954       20
    EXP                 1  control               11.5307      .9537        5
    EXP                 2  masked                 8.5040     2.8504        5
    EXP                 3  uv filter              8.8213     2.6368        5
    EXP                 4  full exposure          3.3760     1.4008        5

  COAT                  2  yes                    4.9933     1.8738       20
    EXP                 1  control                5.3733      .4673        5
    EXP                 2  masked                 5.4693      .4274        5
    EXP                 3  uv filter              6.2613     2.5872        5
    EXP                 4  full exposure          2.8693     1.2127        5
```

Extension to Break (%) (cont.)

```
fabric # and treatment                          Mean     Std Dev    Cases

FAB              6                             9.3898     1.7384      80
  COAT           1  no                         9.1913     1.8714      40
    EXP          1  control                   10.0053     1.0658      10
    EXP          2  masked                    10.3160      .8404      10
    EXP          3  uv filter                 10.0413     1.2046      10
    EXP          4  full exposure              6.4027      .5460      10

  COAT           2  yes                        9.5883     1.5933      40
    EXP          1  control                    9.8387     1.6674      10
    EXP          2  masked                    10.9347      .8919      10
    EXP          3  uv filter                  9.9107      .9116      10
    EXP          4  full exposure              7.6693      .5507      10

FAB              7                            10.6570     2.2880      81
  COAT           1  no                        10.5717     2.0216      41
    EXP          1  control                   11.4347     1.0191      10
    EXP          2  masked                    11.4056     1.4411      12
    EXP          3  uv filter                 11.5133      .7564      10
    EXP          4  full exposure              7.4548     1.3248       9

  COAT           2  yes                       10.7443     2.5557      40
    EXP          1  control                   12.0947     1.9994      10
    EXP          2  masked                    12.1587     2.0511      10
    EXP          3  uv filter                 10.8907     2.0795      10
    EXP          4  full exposure              7.8333     1.4444      10

FAB              8                             8.8587     1.6604      80
  COAT           1  no                         8.6777     1.3641      40
    EXP          1  control                    9.3907      .6819      10
    EXP          2  masked                     9.2960      .4209      10
    EXP          3  uv filter                  9.3840      .9284      10
    EXP          4  full exposure              6.6400      .6335      10

  COAT           2  yes                        9.0397     1.9123      40
    EXP          1  control                   10.5973      .3349      10
    EXP          2  masked                     9.9160      .8377      10
    EXP          3  uv filter                  9.6187      .9424      10
    EXP          4  full exposure              6.0267      .3688      10

  Total Cases = 672
Missing Cases = 113 or  16.8 Pct
```

Energy to Break (J)

```
fabric # and treatment                                   Mean     Std Dev    Cases

For Entire Population                                    .1130     .1260      558

FAB                     1                                .0028     .0025       40
  COAT                  1  no                            .0031     .0027       20
    EXP                 1  control                       .0041     .0025        5
    EXP                 2  masked                        .0053     .0033        5
    EXP                 3  uv filter                     .0022     .0020        5
    EXP                 4  full exposure                 .0009     .0006        5

  COAT                  2  yes                           .0024     .0022       20
    EXP                 1  control                       .0024     .0010        5
    EXP                 2  masked                        .0022     .0017        5
    EXP                 3  uv filter                     .0044     .0033        5
    EXP                 4  full exposure                 .0008     .0003        5

FAB                     2                                .1456     .0971       80
  COAT                  1  no                            .1334     .0889       40
    EXP                 1  control                       .1885     .0563       10
    EXP                 2  masked                        .1756     .0626       10
    EXP                 3  uv filter                     .1669     .0398       10
    EXP                 4  full exposure                 .0027     .0008       10

  COAT                  2  yes                           .1578     .1043       40
    EXP                 1  control                       .2198     .0750       10
    EXP                 2  masked                        .2343     .0658       10
    EXP                 3  uv filter                     .1708     .0271       10
    EXP                 4  full exposure                 .0064     .0013       10

FAB                     3                                .0106     .0098       80
  COAT                  1  no                            .0063     .0067       40
    EXP                 1  control                       .0094     .0085       10
    EXP                 2  masked                        .0095     .0069       10
    EXP                 3  uv filter                     .0057     .0038       10
    EXP                 4  full exposure                 .0007     .0004       10

  COAT                  2  yes                           .0148     .0107       40
    EXP                 1  control                       .0217     .0103       10
    EXP                 2  masked                        .0208     .0080       10
    EXP                 3  uv filter                     .0148     .0071       10
    EXP                 4  full exposure                 .0019     .0006       10
FAB                     4                                .0067     .0056       79
  COAT                  1  no                            .0079     .0052       39
    EXP                 1  control                       .0116     .0057       10
    EXP                 2  masked                        .0091     .0049        9
    EXP                 3  uv filter                     .0078     .0035       10
    EXP                 4  full exposure                 .0033     .0025       10

  COAT                  2  yes                           .0055     .0058       40
    EXP                 1  control                       .0087     .0070       10
    EXP                 2  masked                        .0040     .0025       10
    EXP                 3  uv filter                     .0081     .0067       10
    EXP                 4  full exposure                 .0013     .0020       10

FAB                     5                                .0704     .0858       40
  COAT                  1  no                            .1182     .1006       20
    EXP                 1  control                       .2266     .0453        5
    EXP                 2  masked                        .1179     .0959        5
    EXP                 3  uv filter                     .1237     .0766        5
    EXP                 4  full exposure                 .0044     .0037        5

  COAT                  2  yes                           .0227     .0140       20
    EXP                 1  control                       .0350     .0064        5
    EXP                 2  masked                        .0338     .0089        5
    EXP                 3  uv filter                     .0161     .0054        5
    EXP                 4  full exposure                 .0058     .0052        5
```

Energy to Break (J) (cont.)

```
 fabric # and treatment                           Mean     Std Dev    Cases

FAB                 6                            .0885      .0278       80
  COAT              1  no                        .0814      .0260       40
    EXP             1  control                   .0924      .0124       10
    EXP             2  masked                    .0984      .0128       10
    EXP             3  uv filter                 .0927      .0165       10
    EXP             4  full exposure             .0421      .0098       10

  COAT              2  yes                       .0955      .0281       40
    EXP             1  control                   .0995      .0286       10
    EXP             2  masked                    .1183      .0179       10
    EXP             3  uv filter                 .1018      .0202       10
    EXP             4  full exposure             .0626      .0065       10

FAB                 7                            .2821      .1231       79
  COAT              1  no                        .2526      .0938       39
    EXP             1  control                   .3045      .0466       10
    EXP             2  masked                    .2707      .0649       10
    EXP             3  uv filter                 .3123      .0442       10
    EXP             4  full exposure             .1084      .0280        9

  COAT              2  yes                       .3109      .1415       40
    EXP             1  control                   .3727      .1206       10
    EXP             2  masked                    .3852      .1099       10
    EXP             3  uv filter                 .3354      .1314       10
    EXP             4  full exposure             .1501      .0556       10

FAB                 8                            .2220      .1079       80
  COAT              1  no                        .1783      .0691       40
    EXP             1  control                   .2194      .0307       10
    EXP             2  masked                    .2018      .0269       10
    EXP             3  uv filter                 .2178      .0491       10
    EXP             4  full exposure             .0742      .0188       10

  COAT              2  yes                       .2657      .1220       40
    EXP             1  control                   .3573      .0406       10
    EXP             2  masked                    .3330      ,0421       10
    EXP             3  uv filter                 .2971      .0725       10
    EXP             4  full exposure             .0754      .0109       10

  Total Cases = 672
```

Moisture Regain (%)

```
fabric # and treatment                          Mean     Std Dev    Cases

For Entire Population                          8.9028     .9664      192

FAB                     1                      9.2204     .6789       24
  COAT                  1  no                  9.5975     .6637       12
    EXP                 1  control             9.7767     .7575        3
    EXP                 2  masked              9.9933     .4508        3
    EXP                 3  uv filter           9.6667     .5424        3
    EXP                 4  full exposure       8.9533     .6621        3

  COAT                  2  yes                 8.8433     .4614       12
    EXP                 1  control             9.1200     .8508        3
    EXP                 2  masked              8.8167     .2003        3
    EXP                 3  uv filter           8.5867     .2479        3
    EXP                 4  full exposure       8.8500     .3617        3

FAB                     2                      7.8300     .8581       24
  COAT                  1  no                  8.6408     .1934       12
    EXP                 1  control             8.6067     .2714        3
    EXP                 2  masked              8.6300     .2007        3
    EXP                 3  uv filter           8.8200     .1212        3
    EXP                 4  full exposure       8.5067     .0058        3

  COAT                  2  yes                 7.0192     .2601       12
    EXP                 1  control             7.2267     .4271        3
    EXP                 2  masked              7.0533     .1595        3
    EXP                 3  uv filter           7.0000     .1082        3
    EXP                 4  full exposure       6.7967     .1069        3

FAB                     3                      8.4750     .8372       24
  COAT                  1  no                  9.1058     .5856       12
    EXP                 1  control             9.8300     .5057        3
    EXP                 2  masked              8.9833     .2479        3
    EXP                 3  uv filter           8.9367     .3958        3
    EXP                 4  full exposure       8.6733     .5288        3

  COAT                  2  yes                 7.8442     .5044       12
    EXP                 1  control             7.8233     .6274        3
    EXP                 2  masked              8.0833     .2281        3
    EXP                 3  uv filter           7.5100     .8141        3
    EXP                 4  full exposure       7.9600     .1308        3

FAB                     4                      8.5729     .4936       24
  COAT                  1  no                  8.8033     .6043       12
    EXP                 1  control             9.2300     .4498        3
    EXP                 2  masked              9.1467     .3347        3
    EXP                 3  uv filter           8.1800     .3874        3
    EXP                 4  full exposure       8.6567     .6921        3

  COAT                  2  yes                 8.3425     .1684       12
    EXP                 1  control             8.4533     .1801        3
    EXP                 2  masked              8.4133     .1553        3
    EXP                 3  uv filter           8.2800     .1212        3
    EXP                 4  full exposure       8.2233     .1779        3

FAB                     5                      8.9612     .7621       24
  COAT                  1  no                  9.6092     .3942       12
    EXP                 1  control             9.8833     .4486        3
    EXP                 2  masked              9.3667     .2669        3
    EXP                 3  uv filter           9.4967     .3089        3
    EXP                 4  full exposure       9.6900     .5069        3

  COAT                  2  yes                 8.3133     .3782       12
    EXP                 1  control             8.6667     .0451        3
    EXP                 2  masked              8.3933     .4868        3
    EXP                 3  uv filter           8.0367     .2250        3
    EXP                 4  full exposure       8.1567     .3855        3
```

Moisture Regain (%) (cont.)

```
fabric # and treatment                                 Mean     Std Dev     Cases

FAB                     6                             9.0129     .7718        24
  COAT                  1  no                         9.2658     .9228        12
    EXP                 1  control                   10.3333     .7605         3
    EXP                 2  masked                     9.1800     .5197         3
    EXP                 3  uv filter                  8.2400     .4713         3
    EXP                 4  full exposure              9.3100     .5576         3

  COAT                  2  yes                        8.7600     .5044        12
    EXP                 1  control                    9.0433     .5074         3
    EXP                 2  masked                     8.8967     .3272         3
    EXP                 3  uv filter                  8.4500     .7374         3
    EXP                 4  full exposure              8.6500     .4246         3

FAB                     7                             9.2154     .6360        24
  COAT                  1  no                         9.7733     .3529        12
    EXP                 1  control                    9.7533     .4994         3
    EXP                 2  masked                    10.1467     .1804         3
    EXP                 3  uv filter                  9.7200     .1908         3
    EXP                 4  full exposure              9.4733     .1332         3

  COAT                  2  yes                        8.6575     .2049        12
    EXP                 1  control                    8.7533     .1050         3
    EXP                 2  masked                     8.6000     .2689         3
    EXP                 3  uv filter                  8.7900     .0346         3
    EXP                 4  full exposure              8.4867     .2401         3

FAB                     8                             9.9342    1.0931        24
  COAT                  1  no                        10.9883     .1726        12
    EXP                 1  control                   11.1667     .1904         3
    EXP                 2  masked                    10.9733     .0503         3
    EXP                 3  uv filter                 11.0367     .0306         3
    EXP                 4  full exposure             10.7767     .0737         3

  COAT                  2  yes                        8.8800     .2099        12
    EXP                 1  control                    9.1067     .2214         3
    EXP                 2  masked                     8.9133     .1662         3
    EXP                 3  uv filter                  8.7367     .0208         3
    EXP                 4  full exposure              8.7633     .1877         3

  Total Cases = 336
```

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APPENDIX A-4: Summary Tables of F-Ratios

type of fabric (fabric number):

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL               SSH       SSE       MSH        MSE       F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN                  5004.26     52.05   5004.26       0.19   26149.30      1.0    272.0   0.0
UNIV  COAT                          35.69     52.05     35.69       0.19     188.47      1.0    272.0   .188E-13
UNIV  EXP                         5098.19     52.05   1699.40       0.19    8880.06      3.0    272.0   0.0
UNIV  FAB                         1103.88     52.05    157.70       0.19     824.04      7.0    272.0   0.0
UNIV  COAT*EXP                      81.98     52.05     27.33       0.19     142.78      3.0    272.0   0.0
UNIV  COAT*FAB                     364.47     52.05     52.07       0.19     272.07      7.0    272.0   0.0
UNIV  EXP*FAB                     1547.82     52.05     73.71       0.19     385.14     21.0    272.0   0.0
UNIV  COAT*EXP*FAB                1202.71     52.05     57.27       0.19     299.27     21.0    272.0   0.0
UNIV  CASES(COAT,EXP,FAB)           52.05      ****      0.19       ****       ****    272.0     ****    ****
ERROR TERM: CASES(COAT,EXP,FAB)
```

presence of weighting agent:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL               SSH       SSE       MSH        MSE       F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN                  5004.26   2323.87   5004.26       7.26     689.06      1.0    320.0   0.0
UNIV  COAT                          35.69   2323.87     35.69       7.26       4.91      1.0    320.0   0.02735
UNIV  EXP                         5098.19   2323.87   1699.40       7.26     234.00      3.0    320.0   0.0
UNIV  WEIGHT                       406.95   2323.87    406.95       7.26      56.04      1.0    320.0   .749E-12
UNIV  COAT*EXP                      79.95   2323.87     26.65       7.26       3.67      3.0    320.0   0.01262
UNIV  COAT*WEIGHT                  285.07   2323.87    285.07       7.26      38.50      1.0    320.0 0.424E-8
UNIV  EXP*WEIGHT                   363.24   2323.87    121.08       7.26      16.67      3.0    320.0 0.434E-9
UNIV  COAT*EXP*WEIGHT              913.72   2323.87    304.57       7.26      41.94      3.0    320.0   .898E-13
UNIV  CASES(COAT,EXP,WEIGHT)      2323.87      ****      7.26       ****       ****    320.0     ****    ****
ERROR TERM: CASES(COAT,EXP,WEIGHT
```

presence of dye:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL               SSH       SSE       MSH        MSE       F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN                  5004.26   1951.41   5004.26       6.10     820.62      1.0    320.0   0.0
UNIV  COAT                          35.69   1951.41     35.69       6.10       5.85      1.0    320.0   0.01612
UNIV  EXP                         5098.19   1951.41   1699.40       6.10     278.67      3.0    320.0   0.0
UNIV  DYE                          502.01   1951.41    502.01       6.10      82.32      1.0    320.0   .500E-13
UNIV  COAT*EXP                      81.98   1951.41     27.33       6.10       4.48      3.0    320.0   0.00425
UNIV  COAT*DYE                     298.13   1951.41    298.13       6.10      48.88      1.0    320.0   .198E-10
UNIV  EXP*DYE                      471.31   1951.41    157.10       6.10      25.76      3.0    320.0   .104E-12
UNIV  COAT*EXP*DYE                1048.07   1951.41    349.36       6.10      57.29      3.0    320.0   .110E-12
UNIV  CASES(COAT,EXP,DYE)         1951.41      ****      6.10       ****       ****    320.0     ****    ****
ERROR TERM: CASES(COAT,EXP,DYE)
```

artificially or naturally aged:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL               SSH       SSE       MSH        MSE       F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN                  5004.26   3584.73   5004.26      11.20     446.72      1.0    320.0   0.0
UNIV  COAT                          35.69   3584.73     35.69      11.20       3.19      1.0    320.0   0.07524
UNIV  EXP                         5098.19   3584.73   1699.40      11.20     151.70      3.0    320.0   0.0
UNIV  AGE                           72.31   3584.73     72.31      11.20       6.45      1.0    320.0   0.01156
UNIV  COAT*EXP                      81.98   3584.73     27.33      11.20       2.44      3.0    320.0   0.06444
UNIV  COAT*AGE                     133.30   3584.73    133.30      11.20      11.90      1.0    320.0   0.00064
UNIV  EXP*AGE                       63.62   3584.73     21.21      11.20       1.89      3.0    320.0   0.13063
UNIV  COAT*EXP*AGE                 416.98   3584.73    138.99      11.20      12.41      3.0    320.0 0.106E-6
UNIV  CASES(COAT,EXP,AGE)         3584.73      ****     11.20       ****       ****    320.0     ****    ****
ERROR TERM: CASES(COAT,EXP,AGE)
```

Flexural Rigidity (mg-cm)

type of fabric (fabric number):

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL             SSH        SSE        MSH          MSE      F-RATIO     DFH      DFE    PROB

UNIV  GRAND MEAN               0.2238587  36694.49  0.2238587     163.81  13[illegible].28     1.0    224.0  0.0
UNIV  COAT                     798248.48  36694.49  798248.48     163.81     4871.82     1.0    224.0  0.0
UNIV  EXP                        9552.01  36694.49    3184.00     163.81       19.44     3.0    224.0  .310E-10
UNIV  FAB                      823539.07  36694.49  117648.44     163.81      718.18     7.0    224.0  0.0
UNIV  COAT*EXP                   5230.01  36694.49    1743.34     163.81       10.64     3.0    224.0  0.143E-5
UNIV  COAT*FAB                 560817.81  36694.49   80116.79     163.81      489.07     7.0    224.0  0.0
UNIV  EXP*FAB                    7649.85  36694.49     364.28     163.81        2.22    21.0    224.0  0.00222
UNIV  COAT*EXP*FAB               5359.78  36694.49     255.23     163.81        1.56    21.0    224.0  0.06121
ERROR TERM: CASES(COAT,EXP,FAB)
```

presence of weighting agent:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL             SSH        SSE        MSH          MSE      F-RATIO     DFH      DFE    PROB

UNIV  GRAND MEAN                  653.31     26.44     653.31       0.13     5038.88     1.0    204.0  0.0
UNIV  COAT                         13.11     26.44      13.11       0.13      101.10     1.0    204.0  .117E-13
UNIV  EXP                          18.27     26.44       9.14       0.13       70.48     2.0    204.0  .437E-13
UNIV  WEIGHT                        5.08     26.44       5.08       0.13       39.19     1.0    204.0  0.222E-8
UNIV  COAT*EXP                     16.37     26.44       8.18       0.13       63.12     2.0    204.0  .404E-13
UNIV  COAT*WEIGHT                   2.29     26.44       2.29       0.13       17.70     1.0    204.0  0.00004
UNIV  EXP*WEIGHT                    2.58     26.44       1.29       0.13        9.95     2.0    204.0  0.00008
UNIV  COAT*EXP*WEIGHT               3.18     26.44       1.59       0.13       12.25     2.0    204.0  0.947E-5
ERROR TERM: CASES(COAT,EXP,WEIGHT)
```

presence of dye:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL             SSH        SSE        MSH          MSE      F-RATIO     DFH      DFE    PROB

UNIV  GRAND MEAN                  653.31     35.71     653.31       0.18     3732.82     1.0    204.0  0.0
UNIV  COAT                         13.11     35.71      13.11       0.18       74.89     1.0    204.0  -.868E-15
UNIV  EXP                          18.27     35.71       9.14       0.18       52.20     2.0    204.0  .343E-13
UNIV  DYE                           2.51     35.71       2.51       0.18       14.33     1.0    204.0  0.00020
UNIV  COAT*EXP                     16.27     35.71       8.14       0.18       46.49     2.0    204.0  .398E-13
UNIV  COAT*DYE                      0.68     35.71       0.68       0.18        3.91     1.0    204.0  0.04935
UNIV  EXP*DYE                       0.07     35.71       0.04       0.18        0.20     2.0    204.0  0.81887
UNIV  COAT*EXP*DYE                  0.70     35.71       0.35       0.18        2.01     2.0    204.0  0.13692
ERROR TERM: CASES(COAT,EXP,DYE)
```

artificially or naturally aged:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL             SSH        SSE        MSH          MSE      F-RATIO     DFH      DFE    PROB

UNIV  GRAND MEAN                  653.31     34.13     653.31       0.17     3905.16     1.0    204.0  0.0
UNIV  COAT                         13.11     34.13      13.11       0.17       78.34     1.0    204.0  -.228E-14
UNIV  EXP                          18.27     34.13       9.14       0.17       54.61     2.0    204.0  .987E-14
UNIV  AGE                           3.40     34.13       3.40       0.17       20.36     1.0    204.0  0.00001
UNIV  COAT*EXP                     16.31     34.13       8.15       0.17       48.74     2.0    204.0  .431E-13
UNIV  COAT*AGE                      1.21     34.13       1.21       0.17        7.26     1.0    204.0  0.00785
UNIV  EXP*AGE                       0.47     34.13       0.24       0.17        1.42     2.0    204.0  0.24487
UNIV  COAT*EXP*AGE                  0.40     34.13       0.20       0.17        1.21     2.0    204.0  0.30173
ERROR TERM: CASES(COAT,EXP,AGE)
```

Tensile Strength (N)

type of fabric (fabric number):

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE       PART OF MODEL             SSH         SSE         MSH        MSE      F-RATIO     DFM     DFE     PROB

UNIV  GRAND MEAN               667023.89    15819.58   667023.89      70.31     9487.00      1.0   225.0   0.0
UNIV  COAT                       1882.61    15819.58     1882.61      70.31       26.78      1.0   225.0  0.611E-6
UNIV  EXP                       41396.67    15819.58    13798.89      70.31      196.26      3.0   225.0   0.0
UNIV  FAB                      379536.97    15819.58    54219.57      70.31      771.16      7.0   225.0   0.0
UNIV  COAT*EXP                    388.23    15819.58      129.41      70.31        1.84      3.0   225.0   0.14082
UNIV  COAT*FAB                   7894.14    15819.58     1127.73      70.31       16.04      7.0   225.0  0.199E-8
UNIV  EXP*FAB                   23039.83    15819.58     1097.13      70.31       15.60     21.0   225.0   .379E-33
UNIV  COAT*EXP*FAB               4594.16    15819.58      218.77      70.31        3.11     21.0   225.0   0.00001
ERROR TERM: CASES(COAT,EXP,FAB)
```

presence of weighting agent:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE       PART OF MODEL             SSH         SSE         MSH        MSE      F-RATIO     DFM     DFE     PROB

UNIV  GRAND MEAN                  284.39       31.83      284.39       0.16     1831.89      1.0   205.0   0.0
UNIV  COAT                          0.01       31.83        0.01       0.16        0.06      1.0   205.0   0.79999
UNIV  EXP                          26.02       31.83       13.01       0.16       83.81      2.0   205.0  0.120E-8
UNIV  WEIGHT                        1.89       31.83        1.89       0.16       12.20      1.0   205.0   0.00058
UNIV  COAT*EXP                      0.40       31.83        0.20       0.16        1.29      2.0   205.0   0.27778
UNIV  COAT*WEIGHT                   0.02       31.83        0.02       0.16        0.12      1.0   205.0   0.72900
UNIV  EXP*WEIGHT                    3.44       31.83        1.72       0.16       11.08      2.0   205.0   0.00003
UNIV  COAT*EXP*WEIGHT               0.69       31.83        0.35       0.16        2.24      2.0   205.0   0.10957
ERROR TERM: CASES(COAT,EXP,WEIGHT)
```

presence of dye:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE       PART OF MODEL             SSH         SSE         MSH        MSE      F-RATIO     DFM     DFE     PROB

UNIV  GRAND MEAN                  284.39       33.87      284.39       0.17     1721.14      1.0   205.0   0.0
UNIV  COAT                          0.01       33.87        0.01       0.17        0.06      1.0   205.0   0.80582
UNIV  EXP                          26.02       33.87       13.01       0.17       78.75      2.0   205.0  0.774E-7
UNIV  DYE                           0.80       33.87        0.80       0.17        4.85      1.0   205.0   0.02860
UNIV  COAT*EXP                      0.42       33.87        0.21       0.17        1.28      2.0   205.0   0.28644
UNIV  COAT*DYE                      0.13       33.87        0.13       0.17        0.78      1.0   205.0   0.37938
UNIV  EXP*DYE                       2.42       33.87        1.21       0.17        7.32      2.0   205.0   0.00085
UNIV  COAT*EXP*DYE                  0.60       33.87        0.30       0.17        1.79      2.0   205.0   0.16830
ERROR TERM: CASES(COAT,EXP,DYE)
```

artificially or naturally aged:

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE       PART OF MODEL             SSH         SSE         MSH        MSE      F-RATIO     DFM     DFE     PROB

UNIV  GRAND MEAN                  284.39       37.13      284.39       0.18     1570.32      1.0   205.0   0.0
UNIV  COAT                          0.01       37.13        0.01       0.18        0.06      1.0   205.0   0.81417
UNIV  EXP                          26.02       37.13       13.01       0.18       71.85      2.0   205.0  0.871E-7
UNIV  AGE                           0.07       37.13        0.07       0.18        0.37      1.0   205.0   0.54254
UNIV  COAT*EXP                      0.42       37.13        0.21       0.18        1.17      2.0   205.0   0.31220
UNIV  COAT*AGE                      0.09       37.13        0.09       0.18        0.50      1.0   205.0   0.47827
UNIV  EXP*AGE                       0.34       37.13        0.17       0.18        0.95      2.0   205.0   0.39016
UNIV  COAT*EXP*AGE                  0.23       37.13        0.11       0.18        0.63      2.0   205.0   0.53205
ERROR TERM: CASES(COAT,EXP,AGE)
```

type of fabric (fabric number):

```
HIERARCHICAL     SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSH        SSE        MSH        MSE      F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN             23666.67     361.05   23666.67      1.60    14748.44      1.0    225.0  0.0
UNIV  COAT                       8.50     361.05       8.50      1.60        5.30      1.0    225.0  0.02226
UNIV  EXP                     1166.49     361.05     388.83      1.60      242.33      3.0    225.0  0.0
UNIV  FAB                     6596.54     361.05     942.36      1.60      587.26      7.0    225.0  0.0
UNIV  COAT*EXP                   3.24     361.05       1.08      1.60        0.67      3.0    225.0  0.56882
UNIV  COAT*FAB                 127.60     361.05      18.23      1.60       11.36      7.0    225.0 0.238E-9
UNIV  EXP*FAB                  443.37     361.05      21.11      1.60       13.16     21.0    225.0  .112E-27
UNIV  COAT*EXP*FAB              64.09     361.05       3.05      1.60        1.90     21.0    225.0  0.01194
ERROR TERM: CASES(COAT,EXP,FAB)
```

presence of weighting agent:

```
HIERARCHICAL     SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSH        SSE        MSH        MSE      F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN               268.81       8.88     268.81      0.04     6203.79      1.0    205.0  0.0
UNIV  COAT                       0.03       8.88       0.03      0.04        0.79      1.0    205.0  0.37505
UNIV  EXP                       16.84       8.88       8.42      0.04      194.28      2.0    205.0  .477E-47
UNIV  WEIGHT                     2.23       8.88       2.23      0.04       51.56      1.0    205.0 0.105E-7
UNIV  COAT*EXP                   0.04       8.88       0.02      0.04        0.48      2.0    205.0  0.61696
UNIV  COAT*WEIGHT                0.10       8.88       0.10      0.04        2.32      1.0    205.0  0.12882
UNIV  EXP*WEIGHT                 0.68       8.88       0.34      0.04        7.88      2.0    205.0  0.00052
UNIV  COAT*EXP*WEIGHT            0.23       8.88       0.11      0.04        2.65      2.0    205.0  0.07321
ERROR TERM: CASES(COAT,EXP,WEIGHT)
```

presence of dye:

```
HIERARCHICAL     SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSH        SSE        MSH        MSE      F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN               268.81       9.69     268.81      0.05     5683.69      1.0    205.0  0.0
UNIV  COAT                       0.03       9.69       0.03      0.05        0.73      1.0    205.0  0.39540
UNIV  EXP                       16.84       9.69       8.42      0.05      178.28      2.0    205.0  .138E-44
UNIV  DYE                        1.79       9.69       1.79      0.05       37.83      1.0    205.0 0.128E-7
UNIV  COAT*EXP                   0.05       9.69       0.03      0.05        0.49      2.0    205.0  0.61151
UNIV  COAT*DYE                   0.01       9.69       0.01      0.05        0.25      1.0    205.0  0.61987
UNIV  EXP*DYE                    0.50       9.69       0.25      0.05        5.28      2.0    205.0  0.00583
UNIV  COAT*EXP*DYE               0.18       9.69       0.09      0.05        1.87      2.0    205.0  0.15718
ERROR TERM: CASES(COAT,EXP,DYE)
```

artificially or naturally aged:

```
HIERARCHICAL     SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSH        SSE        MSH        MSE      F-RATIO     DFM      DFE     PROB

UNIV  GRAND MEAN               268.81      11.51     268.81      0.06     4788.88      1.0    205.0  0.0
UNIV  COAT                       0.03      11.51       0.03      0.06        0.61      1.0    205.0  0.43584
UNIV  EXP                       16.84      11.51       8.42      0.06      149.97      2.0    205.0  .745E-40
UNIV  AGE                        0.19      11.51       0.19      0.06        3.40      1.0    205.0  0.06661
UNIV  COAT*EXP                   0.05      11.51       0.03      0.06        0.48      2.0    205.0  0.63317
UNIV  COAT*AGE                   0.23      11.51       0.23      0.06        4.05      1.0    205.0  0.04540
UNIV  EXP*AGE                    0.16      11.51       0.08      0.06        1.62      2.0    205.0  0.20013
UNIV  COAT*EXP*AGE               0.04      11.51       0.02      0.06        0.36      2.0    205.0  0.70141
ERROR TERM: CASES(COAT,EXP,AGE)
```

Energy to Break (J)

type of fabric (fabric number):

```
HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSM        SSE        MSM        MSE       F-RATIO    DFM      DFE      PROB

UNIV   GRAND MEAN                7.13       0.55       7.13 0.2438E-2    2925.73     1.0    224.0    0.0
UNIV   COAT                      0.06       0.55       0.06 0.2438E-2      24.07     1.0    224.0 0.179E-5
UNIV   EXP                       1.07       0.55       0.36 0.2438E-2     146.55     3.0    224.0    0.0
UNIV   FAB                       5.60       0.55       0.80 0.2438E-2     328.16     7.0    224.0    0.0
UNIV   COAT*EXP                  0.02       0.55 0.7872E-2 0.2438E-2       3.23     3.0    224.0    0.02324
UNIV   COAT*FAB                  0.27       0.55       0.04 0.2438E-2      16.06     7.0    224.0  .178E-12
UNIV   EXP*FAB                   0.80       0.55       0.04 0.2438E-2      15.58    21.0    224.0  .674E-32
UNIV   COAT*EXP*FAB              0.12       0.55 0.5674E-2 0.2438E-2       2.33    21.0    224.0    0.00126
ERROR  TERM: CASES(COAT,EXP,FAB)
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presence of weighting agent:

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HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSM        SSE        MSM        MSE       F-RATIO    DFM      DFE      PROB

UNIV   GRAND MEAN              195.48      37.07     195.48       0.18    1075.81     1.0    204.0    0.0
UNIV   COAT                      0.09      37.07       0.09       0.18       0.49     1.0    204.0    0.48553
UNIV   EXP                      40.98      37.07      20.49       0.18     112.75     2.0    204.0  .104E-32
UNIV   WEIGHT                    3.55      37.07       3.55       0.18      19.52     1.0    204.0    0.00002
UNIV   COAT*EXP                  0.07      37.07       0.04       0.18       0.20     2.0    204.0    0.81808
UNIV   COAT*WEIGHT               0.03      37.07       0.03       0.18       0.15     1.0    204.0    0.69779
UNIV   EXP*WEIGHT                0.43      37.07       0.22       0.18       1.19     2.0    204.0    0.30655
UNIV   COAT*EXP*WEIGHT           0.88      37.07       0.44       0.18       2.43     2.0    204.0    0.09085
ERROR  TERM: CASES(COAT,EXP,WEIGHT)
```

presence of dye:

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HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSM        SSE        MSM        MSE       F-RATIO    DFM      DFE      PROB

UNIV   GRAND MEAN              195.48      38.37     195.48       0.19    1039.31     1.0    204.0    0.0
UNIV   COAT                      0.09      38.37       0.09       0.19       0.47     1.0    204.0    0.49297
UNIV   EXP                      40.98      38.37      20.49       0.19     108.95     2.0    204.0  .848E-32
UNIV   DYE                       1.41      38.37       1.41       0.19       7.48     1.0    204.0    0.00679
UNIV   COAT*EXP                  0.08      38.37       0.04       0.19       0.22     2.0    204.0    0.80609
UNIV   COAT*DYE             0.3909E-2      38.37  0.3909E-2       0.19       0.02     1.0    204.0    0.88551
UNIV   EXP*DYE                   0.62      38.37       0.31       0.19       1.65     2.0    204.0    0.19485
UNIV   COAT*EXP*DYE              1.56      38.37       0.78       0.19       4.14     2.0    204.0    0.01735
ERROR  TERM: CASES(COAT,EXP,DYE)
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artificially or naturally aged:

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HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE      PART OF MODEL          SSM        SSE        MSM        MSE       F-RATIO    DFM      DFE      PROB

UNIV   GRAND MEAN              195.48      41.50     195.48       0.20     960.89     1.0    204.0    0.0
UNIV   COAT                      0.09      41.50       0.09       0.20       0.44     1.0    204.0    0.50872
UNIV   EXP                      40.98      41.50      20.49       0.20     100.73     2.0    204.0  248E-13
UNIV   AGE                       0.03      41.50       0.03       0.20       0.15     1.0    204.0    0.69667
UNIV   COAT*EXP                  0.08      41.50       0.04       0.20       0.20     2.0    204.0    0.81828
UNIV   COAT*AGE                  0.27      41.50       0.27       0.20       1.33     1.0    204.0    0.24983
UNIV   EXP*AGE                   0.04      41.50       0.02       0.20       0.10     2.0    204.0    0.90440
UNIV   COAT*EXP*AGE              0.17      41.50       0.08       0.20       0.42     2.0    204.0    0.65651
ERROR  TERM: CASES(COAT,EXP,AGE)
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Moisture Regain (%)

type of fabric (fabric number):

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HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE       PART OF MODEL              SSH       SSE       MSH        MSE     F-RATIO     DFH      DFE     PROB

UNIV  GRAND MEAN                  15217.78     19.84  15217.78      0.15    98183.36     1.0    128.0  0.0
UNIV  COAT                           62.44     19.84     62.44      0.15      402.84     1.0    128.0  .234E-40
UNIV  EXP                             6.59     19.84      2.20      0.15       14.17     3.0    128.0  0.496E-7
UNIV  FAB                            65.29     19.84      9.33      0.15       60.18     7.0    128.0  .178E-38
UNIV  COAT*EXP                        0.51     19.84      0.17      0.15        1.10     3.0    128.0  0.35184
UNIV  COAT*FAB                       13.33     19.84      1.90      0.15       12.29     7.0    128.0  .595E-11
UNIV  EXP*FAB                         4.87     19.84      0.23      0.15        1.50    21.0    128.0  0.08844
UNIV  COAT*EXP*FAB                    5.53     19.84      0.26      0.15        1.70    21.0    128.0  0.03807
UNIV  CASES(COAT,EXP,FAB)            19.84      ****      0.15      ****        ****   128.0     ****     ****
ERROR TERM: CASES(COAT,EXP,FAB)
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presence of weighting agent:

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HIERARCHICAL      SUMMARY TABLE OF F-RATIOS
TYPE       PART OF MODEL              SSH       SSE        MSH          MSE     F-RATIO     DFH      DFE     PROB

UNIV  GRAND MEAN                    133.26      0.39      133.26  0.2920E-2    45625.35     1.0    132.0  0.0
UNIV  COAT                            0.01      0.39        0.01  0.2920E-2        3.55     1.0    132.0  0.06188
UNIV  EXP                             0.02      0.39        0.01  0.2920E-2        3.88     2.0    132.0  0.02318
UNIV  WEIGHT                     0.1383E-2      0.39   0.1383E-2  0.2920E-2        0.47     1.0    132.0  0.49245
UNIV  COAT*EXP                   0.8411E-3      0.39   0.4205E-3  0.2920E-2        0.14     2.0    132.0  0.86602
UNIV  COAT*WEIGHT                0.2187E-3      0.39   0.2187E-3  0.2920E-2        0.07     1.0    132.0  0.78572
UNIV  EXP*WEIGHT                 0.8956E-3      0.39   0.4478E-3  0.2920E-2        0.15     2.0    132.0  0.85788
UNIV  COAT*EXP*WEIGHT            0.2139E-2      0.39   0.1069E-2  0.2920E-2        0.37     2.0    132.0  0.69405
UNIV  CASES(COAT,EXP,WEIGHT)          0.39      ****   0.2920E-2       ****        ****   132.0     ****     ****
ERROR TERM: CASES(COAT,EXP,WEIGHT)
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presence of dye:

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TYPE       PART OF MODEL              SSH       SSE        MSH          MSE     F-RATIO     DFH      DFE     PROB

UNIV  GRAND MEAN                    133.26      0.38      133.26  0.2878E-2    46289.26     1.0    132.0  0.0
UNIV  COAT                            0.01      0.38        0.01  0.2878E-2        3.80     1.0    132.0  0.05001
UNIV  EXP                             0.02      0.38        0.01  0.2878E-2        3.93     2.0    132.0  0.02195
UNIV  DYE                        0.2418E-2      0.38   0.2418E-2  0.2878E-2        0.84     1.0    132.0  0.36124
UNIV  COAT*EXP                   0.8509E-3      0.38   0.4254E-3  0.2878E-2        0.15     2.0    132.0  0.86275
UNIV  COAT*DYE                   0.7887E-3      0.38   0.7887E-3  0.2878E-2        0.27     1.0    132.0  0.60619
UNIV  EXP*DYE                    0.2279E-2      0.38   0.1139E-2  0.2878E-2        0.40     2.0    132.0  0.67380
UNIV  COAT*EXP*DYE               0.4689E-2      0.38   0.2344E-2  0.2878E-2        0.81     2.0    132.0  0.44502
UNIV  CASES(COAT,EXP,DYE)             0.38      ****   0.2878E-2       ****        ****   132.0     ****     ****
ERROR TERM: CASES(COAT,EXP,DYE)
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artificially or naturally aged:

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TYPE       PART OF MODEL              SSH       SSE        MSH          MSE     F-RATIO     DFH      DFE     PROB

UNIV  GRAND MEAN                    133.25      0.38      133.25  0.2887E-2    46142.38     1.0    132.0  0.0
UNIV  COAT                            0.01      0.38        0.01  0.2887E-2        3.59     1.0    132.0  0.06041
UNIV  EXP                             0.02      0.38        0.01  0.2887E-2        3.92     2.0    132.0  0.02221
UNIV  AGE                        0.2406E-2      0.38   0.2406E-2  0.2887E-2        0.83     1.0    132.0  0.36304
UNIV  COAT*EXP                   0.8509E-3      0.38   0.4254E-3  0.2887E-2        0.15     2.0    132.0  0.86315
UNIV  COAT*AGE                   0.4282E-2      0.38   0.4282E-2  0.2887E-2        1.48     1.0    132.0  0.22568
UNIV  EXP*AGE                    0.1547E-2      0.38   0.7739E-3  0.2887E-2        0.27     2.0    132.0  0.76531
UNIV  COAT*EXP*AGE               0.7087E-3      0.38   0.3543E-3  0.2887E-2        0.12     2.0    132.0  0.88482
UNIV  CASES(COAT,EXP,AGE)             0.38      ****   0.2887E-2       ****        ****   132.0     ****     ****
ERROR TERM: CASES(COAT,EXP,AGE)
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